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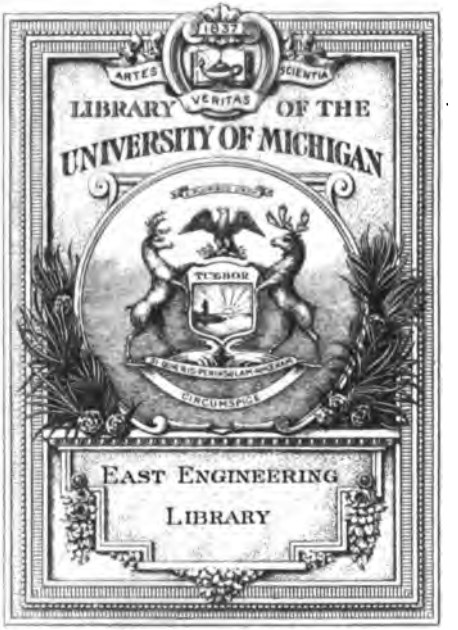
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THE CHEMICAL AND METALLOGRAPHIC EXAMINATION OF IRON, STEEL AND BRASS

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THE CHEMICAL AND METALLOGRAPHIC EXAMINATION OF IRON, STEEL AND BRASS

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PREFACE

The necessity for the chemical analysis of alloys has long been recognized but modern methods of manufacture and the use of metals under conditions of severe strain demand additional information which can best be obtained by the examination of polished specimens. Both of these branches of metal inspection are considered in this book.

Part I deals with the Chemical Analysis of Alloys and includes well tested methods of analysis selected mainly from reports of the United States Bureau of Standards or from papers of the American Society for Testing Materials. Although most of the standard methods of steel analysis are included, special emphasis has been placed on those methods which are both rapid and accurate.

Part II considers the physical rather than the chemical inspection of metals and describes the methods of preparation and examination of polished metal surfaces as an independent means of determining the quality of material as well as an aid in getting representative samples for chemical analysis. A brief introduction to metallography, in so far as it applies to the inspection of alloys, is included.

The authors wish to express their sincere appreciation to Messrs. Bauer and Deiss whose book on the "Sampling and Analysis of Iron and Steel," translated by them in 1915 and published with many additions and modifications suggested the idea of combining chemical and metallographic inspection. A small portion of the translation is included in this book, notably several tables and a number of photomicrographs for which the authors again express their thanks.

Grateful acknowledgement is made to Professor Henry Fay for the use of several photomicrographs and to Dr. W. P. Davey for an X-ray Photograph. Special thanks are due to Mr. V. O. Homerberg who prepared and photographed many of the specimens used in illustration.

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
August, 1921.

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THE CHEMICAL AND METALLOGRAPHIC EXAMINATION OF IRON, STEEL AND BRASS

PART I

THE CHEMICAL ANALYSIS OF IRON, STEEL AND BRASS

PART I

THE CHEMICAL ANALYSIS OF IRON, STEEL AND BRASS

CHAPTER I

INTRODUCTION

The importance of iron and steel in daily life has led to the study of the influence of every chemical element likely to occur in such materials either as intentional ingredient or as unintentional impurity. This study has involved the making of countless chemical analyses and the testing of many methods. The preponderance of the element iron influences the method of procedure and often, when only small quantities of certain elements are likely to be present, the best results are obtained by methods quite unsuitable for the exact determination of large quantities of these elements.

The elements likely to be found in ferrous alloys may be classified into three groups with respect to the frequency with which the chemist is required to test for them. The first group includes the elements carbon, manganese, phosphorus, silicon and sulfur. They are present in nearly every sample of iron and steel. Both the maker and user are interested to know how much of each is present and often the material is valueless for certain purposes unless the quantities are found to lie within fairly narrow limits. The quantitative determination of the content of these elements, therefore, constitutes the regular routine work of every chemist engaged in the analysis of iron and steel. The actual iron content of commercial iron and steel, on the other hand, is not usually determined by direct chemical analysis because it is easier, and in many cases more accurate, to assume that the element iron constitutes the remainder of the metal. The above five elements are quite unlike one another in their chemical characteristics. They will be discussed in alphabetical order.

The second group includes the elements copper, chromium, iron, nickel, molybdenum, tungsten and vanadium. Except iron, these elements do not occur to an appreciable extent in most samples of iron and steel but they are important constituents of some special or so-called *alloy steels* and it is important that every chemist should know how to detect them qualitatively and to determine them quantitatively. When the iron content of the metal is less than about 98 per cent, it is best to determine the quantity by careful chemical analysis as it is not always safe to assume that it can be determined "by difference." The chemical properties of the first four members of this group, also arranged in alphabetical sequence, are known to every chemist. The properties of the last three elements are not so well known because they are not always discussed fully in courses of chemical instruction given at our colleges and technical schools. They play an important part in modern "high-speed" steels so that they can no longer be regarded as rare elements.

The third group includes aluminium, arsenic, cobalt, titanium nitrogen and oxygen. These elements are likely to occur in iron and steel and many authorities feel that they influence the properties of the metal to a marked degree. The quantities present are usually small and there is often considerable difficulty in making the analysis with satisfactory accuracy. It is known, for example, that the presence of *oxides* is likely to cause the development of flaws in steel but it is usually easier to detect oxide inclusions by microscopic examination than by chemical analysis. The average oxygen content of the metal may be low but at one particular place there may be enough slag to cause trouble.

The methods to be described for the analysis of iron and steel will be discussed according to the above grouping. In most cases a number of methods will be given, all of which have proved capable of yielding accurate results. Next, will follow a chapter on electrometric methods for analyzing steel. These methods are grouped separately partly because special equipment and different technique are required and partly because it is too soon to predict to what extent they will replace the better known methods of quantitative analysis. Finally, a chapter will be added describing methods of analysis of important

commercial alloys, such as brass and bronze, in which iron is not usually an intentional constituent and which are known as "non-ferrous" alloys.

So many good methods are known for the analysis of iron and steel that it is difficult to say which method is best. According to the general custom in text books on analytical chemistry, it would seem natural to discuss gravimetric methods first, then volumetric or titration methods and finally electrolytic, colorimetric or other special methods. The objection to this treatment lies in the fact that emphasis is likely to be placed upon methods which are seldom used in practice. The chemical balance is the basis of all exact chemical measurement and, for this reason, it is usually assumed that the most accurate methods are those in which the final result is obtained by weighing some pure compound. For determining small quantities of substances, however, it is often far more accurate to obtain the final result by titration or by comparing a color with certain standards. By this means the presence of quantities which cannot be weighed on an ordinary chemical balance can be detected and determined with precision. An attempt will be made, to classify the methods with respect to their usefulness. This appears very simple on the surface and it would be were it true, as chemists sometimes assume, that there is always one best method for making each analysis. An experience of over 20 years in inspecting the results of young chemists has shown that there is individual taste in chemistry as in other things. Chemists like and dislike chemical methods with the same freedom of impulse that they show in liking and in disliking people. Some chemists are able to get good results by methods which do not find favor with others. Again, a relatively inexperienced person may become very expert in making a certain kind of chemical analysis and yet his judgment with regard to the relative values of methods may be faulty. Often the reason a chemist dislikes a certain method is due to a slight misunderstanding of some particular point.

Probably no two chemists would agree absolutely with respect to the relative reliabilities of the various methods to be described. In many cases the choice will vary with respect to the nature of the material examined. In Germany, the Volhard method appears to be the favorite one for the determination of manganese

in iron and steel, in this country A. A. Blair and others have advocated the use of the "bismuthate" method while in many other laboratories the "persulfate" method is preferred for determining small quantities of manganese and the Volhard method is used for larger quantities. Again, in the case of carbon, it is possible to get excellent results by a variety of procedures. In Germany the Corleis chrome-sulfuric acid method is well-liked but equally good results can be obtained in a fraction of the time by means of direct combustion in the electric furnace. In deciding upon the relative usefulness of methods, due respect will be paid to the recommendations of the American Society, for Testing Materials and to the work done by the Bureau of Standards at Washington, D. C. It should be borne in mind, however, that all chemists and all methods are fallible, and it is just as desirable to check up results in doubtful cases by different methods as it is to have the work checked by another chemist. It is one of the most discouraging happenings in the life of a chemist to have something go wrong for an unsuspected reason. Sometimes the trouble is caused by impure reagents, sometimes by the presence of an unsuspected element and sometimes by a slight error in manipulation.

This book is written more from the point of view of the educator than from that of the busy analyst. A person who can blindly follow directions in the laboratory without understanding the nature of the chemical reactions involved is not a chemist any more than is the housewife who follows the directions of the cook book and gets good results in the chemical reactions of cooking. In the long run, the chemical worker becomes more efficient and more reliable when he knows what he is doing and why he is doing it. To be sure, the man who knows less is sometimes willing to work for less and for this reason employers are often willing to employ ignorant labor. Sometimes such persons do very conscientious work in the chemical laboratory and obtain excellent results. It is easier to teach a man to weigh and to read a burette than it is to make a scholar. This book is not written for the chemical laborer so much as for the man who wants to know and to understand methods of chemical analysis.

CHAPTER II

CARBON

Carbon occurs in iron and steel in the combined form as carbide, as a solid solution of iron carbide in iron, and in the uncombined state as graphite or as temper carbon.

Absolutely reliable methods for the determination of combined carbon in the presence of free carbon are not known but it is possible to determine the total carbon and that which is uncombined. In order, therefore, to determine the amount of combined carbon in a sample, the total carbon and free carbon are determined separately and the combined carbon found by difference.

Graphite and temper carbon cannot be separated by chemical means. It is possible in many cases, by means of the metallographic method described in the Part II of this book, to find out whether the free carbon is present as graphite or as temper carbon.

Iron carbide, Fe_3C, is often called *cementite.* It occurs in all annealed steels and in irons which have been chilled in passing from the liquid to the solid state (white cast iron). The eutectoid mixture of cementite and free iron is called *pearlite.* Pearlite contains approximately 0.85 per cent C and steels with less carbon are called *hypo-eutectoid* and with higher carbon they are *hyper-eutectoid.* When quenched above the critical temperature, the iron carbide remains dissolved in solid iron and the solid solution according to its nature and appearance, is known as *austenite, martensite, troostite,* or *sorbite.* These represent different conditions of the solid solution. In cast irons at the temperature of about 1,000°C., and particularly when the silicon content is high, the iron carbide breaks down into iron and graphite (gray cast iron). Temper carbon is formed by heating irons rich in cementite to about 1,000° in the production of malleable cast iron. It is sometimes found in annealed,

high-carbon steel. The structure of iron and steel is discussed more fully in Part II.

Graphite and temper carbon are not affected by boiling, dilute mineral acids. Hot, concentrated nitric acid has a slow oxidizing effect upon them, the graphite flakes being harder to attack than the temper carbon. The latter also burns more readily in oxygen.

Dilute hydrochloric or sulfuric acid decomposes iron carbide with the evolution of more or less hydrocarbon so that the hydrogen evolved on treating iron or steel with these acids is always contaminated with hydrocarbons. When a sample of steel is treated with cold, dilute *nitric* acid, the iron dissolves and the iron carbide is left behind as a brown flocculent residue which goes into solution at about 80°, giving a dark color to the solution which is roughly proportional to the carbide content of the steel. (Colorimetric Method, often used in routine work.) The iron carbide held in solid solution by the iron, or, in other words, that present as austenite, martensite, and even in troostite or sorbite which many consider as colloidal solutions, is somewhat more soluble in nitric acid than the free cementite. It can be distinguished, roughly, from free cementite by the fact that it will dissolve in dilute nitric acid upon shaking at ordinary temperatures. It also imparts a brown color to the nitric acid solution and the color is not quite identical with that produced by the same percentage of carbon present as free cementite in the metal.

Besides iron carbide, Fe_3C, carbides of manganese, chromium, tungsten, molybdenum and vanadium are also found in certain steels.

DETERMINATION OF TOTAL CARBON

Experts in metallographic work can often estimate the carbon content of fully-annealed steel fairly closely by microscopic examination. All accurate chemical methods for determining the total carbon content of a metal depend upon the oxidation of the carbon to carbon dioxide. This oxidation may be accomplished by heating in a furnace in a stream of oxygen or it may be effected in the *wet way* by treating with acid and a very strong oxidizing solution. When the combustion takes place in the furnace, it was for a long time considered advisable to remove most of the iron first. Thus Wöhler (1869), heated the metal

in a stream of pure chlorine gas whereby iron, silicon, phosphorus, sulfur, and certain other elements that are occasionally present, were converted into volatile chlorides leaving behind all the carbon and a small quantity of non-volatile chloride. The silicon present in the slag is also unaffected by this treatment. Berzelius recommended dissolving out the iron by means of a solution containing cupric and ammonium chlorides and Richter replaced the ammonium chloride with potassium chloride because the former is likely to contain a little pyridine chloride. For years this double salt, $2KCl.CuCl_2.2H_2O$, often called in steel laboratories the *double chloride*, was generally used for the preliminary treatment of iron and steel when the total carbon was to be found by dry combustion. Experience showed that it was desirable to have some free hydrochloric acid present.

This preliminary treatment with double chloride requires considerable time and for that reason, probably, the wet combustion method became popular, particularly in Europe. With the advent of the electric furnace, however, and the more accurate study of the temperature necessary to accomplish complete combustion, it was soon found that carbon determinations with the highest possible degree of accuracy can be accomplished by direct combustion, *i.e.* by heating the original sample of metal in oxygen without any preliminary treatment except that of getting it into sufficiently small-sized particles. It is difficult to oxidize completely a very large lump of metal but it is not necessary, or even desirable to reduce the material to the size of coarse-grain powder.

After the solid carbon has been oxidized to gaseous carbon dioxide, the next step is to absorb the gas by some suitable alkaline reagent. Potassium hydroxide solution, solid soda-lime, asbestos impregnated with sodium hydroxide and barium hydroxide solution are the common absorbents used. Sodium hydroxide solution is not as satisfactory as potassium hydroxide solution because of the insolubility of sodium bicarbonate. As regards the relative advantages of the above four reagents as absorbents for carbon dioxide gas, opinions differ. Certainly soda-lime, when in the proper condition, is as good as any but there are three disadvantages arising from its use. (1) It is not always easy to tell from the appearance of the reagent

whether it is in the proper physical and chemical condition. Sometimes the sample as purchased is practically worthless for exact quantitative work. (2) It does not of itself give any indication of the rate at which the gas is passing through the tube containing it. Sometimes the combustion tube will crack and nearly all of the gas escape without the operator being aware of the fact. (3) To tell whether the first soda-lime is absorbing all of the carbon dioxide it is necessary to use at least two weighed tubes. The tubes are used repeatedly until a gain in weight is noticed in the second tube, when the first tube is refilled and used as the second tube. This necessitates the weighing of two tubes before and after each combustion. Many of these objections to the use of soda-lime are overcome by the use of asbestos impregnated with solid sodium hydroxide as described in Method 2. Caustic potash solution in a suitable absorption bulb, usually of the type recommended by Geissler, can be used repeatedly until a precipitate of potassium bicarbonate appears and a satisfactory absorption can be accomplished with one bulb if the flow of gas is not too rapid. Absorption in a Geissler bulb is not satisfactory when the combustion is conducted rapidly, as in some of the modern laboratories, because the absorption may be incomplete and some of the water from the solution may be swept pass the drying agent at the end of the bulb.

When soda-lime or potassium hydroxide solution is used as absorbent, the carbon content of the original metal is computed from the gain in weight produced by the absorbed carbon dioxide. With barium hydroxide, there are four other methods of arriving at the same result. (1) The precipitated barium carbonate may be filtered off, heated in a crucible and weighed. (2) A definite volume of barium hydroxide of known concentration may be used as absorbent and subsequently the loss in alkalinity due to formation of barium carbonate determined by titrating with dilute acid using phenolphthalein as indicator. (3) The barium carbonate may be filtered off and analyzed by titration with dilute acid, using methyl orange as indicator. (4) The barium hydroxide content of a measured quantity of the solution may be determined before and after the combustion by measuring the electrical resistance of the solution. This last method will be described in Chap. XIX.

1. DETERMINATION OF CARBON BY DIRECT COMBUSTION IN OXYGEN

METHOD OF J. R. CAIN AND L. C. MAXWELL[1]

Principle.—The carbon dioxide obtained by direct combustion is absorbed by barium hydroxide solution; the precipitated barium carbonate is filtered off, dissolved in a measured quantity of standard hydrochloric acid and the excess of the latter titrated with standard alkali, using methyl orange, as indicator.

The use of barium hydroxide as absorbent was suggested by Pettenkofer[2] for the analysis of air and the practice has been applied to the determination of carbon in iron and steel.[3] For a long time, however, the method received little attention in the standard text books on iron and steel analysis. In 1913 about 40 per cent of the prominent American laboratories used barium hydroxide but in most cases the resulting barium carbonate was weighed.

Apparatus.—*Furnace.*—Any apparatus may be used, whether heated by gas or electricity, which will permit heating the sample in oxygen at about 1,100°C. Thus the various forms of tubulated platinum crucibles are suitable but expensive.[4] An electric furnace of the resistance type is recommended.

Such a furnace can be purchased or it may be made by winding an alundum core with nichrome wire and surrounding it with sufficient insulating material to prevent loss of heat. The furnace should be 8 to 12 in. long and capable of holding a combustion tube about 1.5 in. in diameter. It should be capable of operating continuously at not less than 1,063° (m.p. of pure gold). The furnace should be equipped with a rheostat so designed with respect to the line voltage that the proper temperature will be obtained with nearly all the rheostat resistance inserted. As the furnace is used, the nichrome windings deteriorate and the resist-

[1] Bureau of Standards, *Technologic Paper* No. **33**. *Am. Soc. Testing Materials*, **1915**, 201. CAIN and MAXWELL, *J. I. E. C.*, **10**, 520 (1918); **11**, 852 (1919).

[2] *J. pr. Chem.*, **82**, 32 (1861).

[3] PETTERSON and SMITH, *Ber.* **23** (1401); *Z. Anal. Chem.*, **32**, 385. AUPPERLE, *J. Am. Chem. Soc.*, **28**, 858. MCFARLANE and GREGORY, *Chem. News*, **94**, 133.

[4] cf. SHIMER, P. W., *J. I. E. C.*, **1**, 738 (1909).

ance of the furnace increases so that more current must be used. To avoid overloading the furnace it is best to have an ammeter in the circuit; with the 110-volt circuit, about 4 amperes should be sufficient for running the furnace.

The furnace may be used with a standard thermo-couple or may be calibrated with the aid of a thermo-couple so that the operator can judge the approximate temperature by the ammeter reading. The simplest method to check the temperature of the furnace is by means of the melting point of pure gold. Flatten out a piece of this metal, place it on a clean porcelain or alundum boat and leave it in the hot furnace for 10 min. If the gold does not melt, the temperature is low. The same piece of gold may be used repeatedly if it is placed on a clean surface of porcelain or alundum each time.

Combustion Tubes.—With the electric furnace, the combustion itself takes place in a tube about 24 in. long and 1 in. in diameter. The tube may be made of quartz or porcelain, glazed on one or both sides. Quartz sometimes becomes devitrified and porous when used continuously. Platinum tubes are good but the cost is prohibitive. To protect the tube from spattered oxides, a sleeve of sheet nickel (ignited till free from carbon) should be provided. This should be longer than the combustion boat and be placed in the center of the tube.

Catalyzer.—In the front end[1] of the combustion tube, place a roll of copper gauze about 3 in. long and large enough to fill the tube. It should not be placed far enough into the furnace so that there is danger of its melting. It should be heated to about 250°. On heating in oxygen, the copper becomes changed to cupric oxide, CuO, which serves as a catalyzer to insure the complete combustion of the carbon and it also acts as a retainer of any sulfuric acid that may be formed from the sulfur of the iron or steel. If much copper sulfate accumulates in the tube, the catalyzer should be renewed.

Instead of copper oxide, platinized quartz or asbestos may be used. Deiss recommends placing a loose plug of ignited asbestos

[1] The various parts of the apparatus when united form a *train*. The flow of the gas is assumed to take place from back to front and the front, or foward end, is where the gas leaves the train. In most drawings, the front end is shown on the right.

in the tube at the front end of the furnace, and in front of the plug in the projecting tube he uses a 2-in. layer of copper oxide and an equally long layer of a mixture of 9 parts potassium chromate and 1 part of potassium dichromate which has been previously melted in a porcelain crucible and then reduced to coarse powder. Fay[1] recommends as catalyzer a 2-in. roll of ignited asbestos wrapped in nickel gauze. A similar roll placed in the back of the furnace helps to protect the rubber stoppers from radiated heat. To decrease the dead space in the furnace, it is well to place a piece of large glass rod in front of the catalyzer.

Boats.—The iron or steel sample to be analyzed is placed on an open vessel called a *combustion boat.* Suitable boats made of porcelain, quartz, alundum, clay or platinum may be purchased. Nickel boats may be made by cutting a piece of sheet nickel at the corners and bending these up. Such boats are inexpensive. To protect the boat from the action of melted iron oxide, a little alundum sand is placed in it as lining and the iron or steel placed on the alundum.

Absorption Tube.—A Meyer tube having 8 or 10 bulbs, each of 10 or 15 c.c. capacity, is recommended. When such a tube is filled with barium hydroxide solution, the absorption of the carbon dioxide takes place satisfactorily even when the gas is passing through quite rapidly. In front of the Meyer bulb it is best to place a soda-lime tube to protect the barium hydroxide from the carbon dioxide in the atmosphere.

Purification Train.—This method eliminates the necessity of a purifying train in front of the furnace as no precautions are necessary to prevent moisture or sulfur trioxide getting into the barium hydroxide solution. With oxygen of good quality it is not necessary to have the gas purified before it enters the furnace. Sometimes, however, there is a little organic matter in the oxygen. To remove this, pass the gas through a 12-in. porcelain tube containing granular copper oxide and heated to about 900°. In front of this tube place a soda tower filled with soda-lime or stick caustic soda.

Solutions Required.—*Tenth-normal Hydrochloric Acid.*—Use 8 c.c. of concentrated hydrochloric acid (d. 1.1 = approximately 12-normal) per liter. After thoroughly mixing the diluted

[1] "An Advanced Course in Quantitative Analysis," p. 60.

acid, standardize it against pure sodium carbonate, (Gay-Lussac) made by heating pure sodium bicarbonate at 270 to 300° for ½ hr. and cooling in a desiccator; against sodium oxalate (Sörensen) which after being weighed out is converted into sodium carbonate by carefully heating in a platinum crucible over a small flame with the bottom of the crucible a dull red; or by the following precipitation method. Carefully measure out at least 20 c.c. of the acid, dilute with water to a volume of 50–60 c.c. and add a slight excess of approximately-tenth-normal silver nitrate solution. Digest at 70 to 90° until the supernatant liquid is clear and then filter through a weighed Gooch crucible. Wash the precipitate with water containing 2 per cent of 6-normal nitric acid until a portion of the filtrate shows no test for silver when treated with a drop of hydrochloric acid. Dry to constant weight at about 130°. Duplicate determinations should agree within 0.0005 g. of silver chloride.

Methyl Orange.—Dissolve 0.02 g. of the dyestuff in 100 c.c. of hot water and filter when cold.

Tenth-normal Sodium Hydroxide.—Dissolve 4 g. of pure caustic soda in each liter of solution. When methyl orange is to be used as indicator, it is not necessary to protect the sodium hydroxide from the carbon dioxide of the atmosphere, because one molecule of sodium carbonate has the same neutralizing effect as one molecule of sodium hydroxide. Standardize the sodium hydroxide by titrating portions of at least 20 c.c. against the hydrochloric acid solution. To obtain concordant results it is necessary to work with a small quantity of methyl orange (about 1 drop) and always at about the same dilution. Moreover, it is best to match the color of the end-point with that produced by adding less than 1 drop of the acid to the same volume of distilled water as that of the titrated solution.

Barium Hydroxide Solution.—Dissolve 25 g. of barium hydroxide, $Ba(OH)_2.8H_2O$, in each liter of water. Allow the well-mixed solution to stand 2 days and then siphon off the clear liquid through a filter into a large stock bottle. The bottle should be placed on a shelf and be provided with a soda-lime tube to protect it from the carbon dioxide in the atmosphere. (See Fig. 1.) The stopcock on the siphon tube should be protected by a rubber stopper when not in use so that it will not

become clogged with barium carbonate. Enough barium hydroxide solution should be used in the analysis so that each small bulb of the Meyer tube is filled and half of the larger exit bulb.

After setting up the apparatus it must be tested carefully for leaks. The combustion tube should next be heated while oxygen is passed through it to destroy all organic matter. A blank run should then be made in exactly the same way as in the analysis of a weighed sample and the final titration ought not to show more than 0.0001 g. of carbon.

FIG. 1.

Procedure.—Place a layer of alundum sand in the combustion boat and give it a preliminary heating in the furnace before weighing out the sample. Then, with the furnace at the proper temperature and the filled Meyer tube in place, withdraw the boat by means of a stout wire bent to form a hook and allow it to cool until its temperature is just below a visible red. This will not cause loss of carbon unless the particles of metal are less than 60-mesh in size. Satisfactory results are obtained with chips that will just pass through a 10-mesh sieve. Transfer the weighed sample to the boat, quickly push it into the proper place in the furnace and insert the stopper at the back end of the furnace. With metal containing about 1 per cent of carbon or less, use 2 g. of samples and only 1 g. if the carbon content is higher.

Allow the sample to heat for 1 min. in the furnace without passing oxygen into the tube. (During this minute a second sample of steel can be weighed out.) Then begin to pass oxygen into the tube at the rate of 300 to 400 c.c. per minute, taking care that the rate of flow at the front end of the tube is not greater than 225 c.c. per minute, as otherwise the absorption of the carbon dioxide will be incomplete. The combustion of 2 g. of iron requires approximately 600 c.c. of oxygen. In this method it is desired to accomplish complete oxidation of the sample in about 2 min. so that it is important to supply the oxygen rapidly at the start. The gas should be kept bubbling through the Meyer bulb. The rate of flow at the front end of the furnace should never exceed 200 c.c. per minute. By placing a glass capillary tube in

the rubber stopper at the front end of the furnace the escape of gas from the tube is hindered. A plug of glass wool should be placed back of the capillary. With this arrangement the flow of gas into the furnace is cut down automatically as soon as the combustion of the sample is complete.

At the end of 5 min. the Meyer tube may be disconnected and the boat allowed to cool sufficiently for introducing another sample.

Pour off the contents of the Meyer bulb into a Büchner funnel fitted to a suction flask and containing two 7- cm. filter papers, one on top of the other. Wash out the tube three times with distilled water that has been boiled to remove carbon dioxide and cooled in at an atmosphere free from carbon dioxide (by causing all air that comes in contact with it to pass through a soda-lime tube). Then wash the filter four times, taking care that the top of the funnel is washed at the same time.

To the rinsed Meyer tube add from a burette about 5 c.c. more of the tenth-normal hydrochloric acid than is necessary to dissolve all the barium carbonate. Transfer the acid from the Meyer tube to a wide-mouthed flask into which also place the filter papers containing a part of the precipitate. Rinse out the Meyer tube with two portions of the boiled water. It may then be filled with fresh barium hydroxide solution and is ready for another determination. Heat the flask containing the acid on the hot plate until all of the barium carbonate has dissolved. Avoid long heating, however. Titrations are conveniently made when several flasks are ready.

Cool the solution, if necessary, and titrate with standard sodium hydroxide with methyl orange as indicator.

Computation.—One liter of normal acid, or alkali, is equivalent to 67.00 g. of pure sodium oxalate, 53.00 g. of pure sodium carbonate or 143.3 g. of silver chloride. If t c.c. of hydrochloric acid solution were found in the standardization to be equivalent to a g. of sodium oxalate, sodium carbonate or silver chloride, according to the method of standardization, then

$$N_A = \frac{a}{t.e}$$

in which N_A represents the concentration of the acid in terms

of a normal solution, e is 0.067 for sodium oxalate, 0.053 for sodium carbonate or 0.1433 for silver chloride, according to the method of standardization.

If, in titrating the acid against the base, it is found that r_1 c.c. of acid are equivalent to r_2 c.c. of the base, then the concentration of the sodium hydroxide in terms of a normal solution is shown by the expression

$$N_B = \frac{r_1}{r_2} N_A$$

One liter of normal acid, or alkali, is equivalent in this method to 6.00 g. of carbon, or 1 c.c. = 0.00600 g. C. If, then, n_1 c.c. of acid and n_2 c.c. of base are used in the titration of the barium carbonate precipitate from s g. of material, we have

$$\text{Per cent C} = \frac{\left(n_1 - n_2 \frac{r_1}{r_2}\right) 0.6 N_A}{s}$$

If the acid and alkali are both exactly tenth-normal, and exactly 2 g. of metal were used (accurate to within 0.01 g.) then, using the above notation,

$$\text{Per cent C} = 0.3\ (n_1 - n_2)$$

NOTES.—It is absolutely essential in this method to admit the oxygen very fast while the sample is burning and to have the temperature of the furnace near 1,100°C. The laboratory atmosphere must be reasonably free from carbon dioxide; this requirement is easily satisfied if the ventilation is good and there are no gas burners burning in a confined space. In case the ventilation is not good, it is better to use the longer method outlined below.

The method has been found to give accurate results and Cain claims that one operator can make 50 determinations in an 8-hr. working day.

Cain and Maxwell[1] have also worked out an electrolytic resistance method which is still more rapid. The electric resistance of barium hydroxide solutions varies very appreciably with the concentration.

[1] *J. I. E. C.*, **11**, 852. The necessary equipment can be obtained from Arthur H. Thomas Co., Philadelphia.

The absorption apparatus used in this electrical method is essentially a Meyer bulb capable of holding 200 c.c. of solution. The entrance bulb is modified so that a sensitive thermometer and a pair of platinized electrodes can be introduced. By means of a Weibel galvanometer and a specially constructed bridge, the electric resistance can be determined with the aid of an ordinary (60 or 25-cycle) alternating current. A nomographic chart has been worked out in such a way that the concentration of the barium hydroxide solution can be found as soon as the electric resistance and temperature are known. In carrying out a series of analyses at the Bureau of Standards, the average time per analysis was 5 min. Further details are given in Chap. XI.

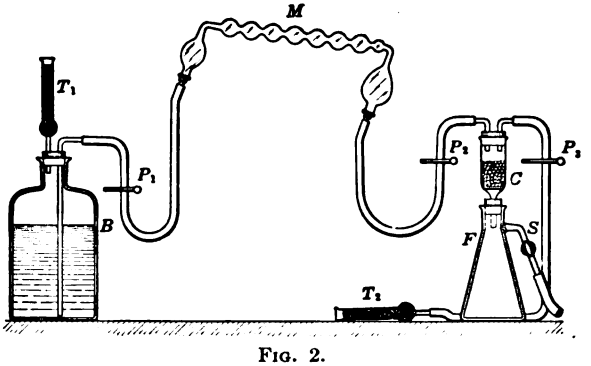

FIG. 2.

Cain's original method, which was adopted by the American Society for Testing Materials as a standard in 1914, did not provide for the preheating of the boat, the furnace was heated only to 1,000 to 1,050° and the oxygen was introduced at a moderate rate for 20 to 25 min. If the oxides were not well fused at the end of this time, they were crushed and reburned. The barium carbonate was filtered off under an atmosphere free from carbon dioxide as follows:

Connect the absorption bulb as shown in Fig. 2. *S* is a two-way stopcock connected with suction. The bubble tube (Meyer tube) is fitted with two rubber stoppers through which short pieces of glass tubing pass. The filter *C* contains a perforated porcelain plate at the bottom; it should slip easily up and down the funnel. Cover the porcelain plate with a felt of asbestos,

which has been cleaned by heating several hours with strong hydrochloric acid and then by washing free from acid. Place on top of this a layer of similarly cleansed quartz to the height shown in the drawing. A mixture of grains such that about one-half passes through a 20-mesh sieve and the remainder through a 10-mesh sieve is suitable. Instead of using the quartz alone, a mixture of quartz and asbestos works well. Fill the funnel with a suspension of asbestos and then wash the quartz into the funnel by means of a strong jet of water from the wash bottle, while maintaining gentle suction. In this way a filter may be prepared which is efficient and yet works rapidly.

Insert the stopper in the funnel and connect it with the Meyer tube as shown in the drawing and apply very gentle suction. When necessary open P_3 to admit air back of the liquid after the contents of the tube have all been transferred to the filter bottle, half fill the large bulb nearest B with water by opening the pinchcock P_1; operate the stopcock S during this and the subsequent operations so as to maintain gentle suction. Manipulate the tube M so as to bring the wash water in contact with all parts of the interior and then suck out the water through C; during this and the subsequent washings leave the pinchcock P_2 open. After eight washings, allowing the wash water to drain off thoroughly each time, detach M and complete the washing by filling C to the top with water free from carbonic acid, sucking dry and repeating the operation once more. Now admit air through the side opening of S, take away C, and transfer the contents of the filter funnel to an Erlenmeyer flask for the titration.

Add an excess of the standard acid from a burette and titrate the excess of alkali in the cold with standard sodium hydroxide, using methyl orange as an indicator.

2. DIRECT COMBUSTION OF CARBON IN OXYGEN—RAPID METHOD

If a sample of steel is placed in a hot furnace it is possible to complete the combustion and convert all of the carbon to carbon dioxide in less than 2 min. provided an adequate supply of oxygen is furnished. For the combustion of 1 g. of steel approximately 300 c.c. of oxygen are required, measured at the laboratory temperature. It is possible to regulate the supply of oxygen so that

the rate at which the gas issues from the front end of the furnace is not rapid at any time but it is advisable to use an absorption tube which is efficient even when a rapid current of gas is passed through it. The absorption bulbs shown in Figs. 3, 4, and 5 have proved efficient.[1]

FIG. 3.

FIG. 4.

FIG. 5.

[1] The illustrations are reproduced by permission from the catalog of the Arthur H. Thomas Co. They also furnish directions for filling the bulbs. The name *ascarite* has been given to asbestos impregnated with sodium hydroxide according to the formula of Stetser and Norton. The original Midvale tube was designed by H. L. Fevert of the Midvale Steel Company. To fill either of the Midvale bulbs, put in about ½-in. layer of glass wool to prevent stoppage of outlet tube, then add ascarite until bulb is almost full. It is suggested that the absorbent be tamped down lightly with a straight piece of wire. According to the designers, the bulb is used with the outlet end of the Vanier combustion train, *i.e.*, with the Vanier zinc tube and Vanier sulfuric acid bulb. A dryer is unnecessary, as the absorbent has the same drying power as fresh c. p. sulfuric acid. One bulb should absorb about 10 g. of CO_2. The outlet end of the combustion tube should be filled for about 3 in. with asbestos previously ignited, otherwise the sample will run high. The first three or four samples are apt to run low. To fill the Fleming bulb, pack the small diameter portion of the upper chamber and the upper stopper with asbestos and the remaining space with phosphoric anhydride; fill the lower chamber with soda-lime containing 2 per cent moisture in 20, 40 and 60-mesh size in alternate layers of about ⅛ in. The lower stopper and the lower portion of the soda-lime chamber are packed loosely with asbestos. The tubes should be used in pairs so that one serves as a tare in weighing the other.. A pair of tubes insures the operator of at least 140 combustions. Ascarite can be used in this bulb in place of the soda-lime.

The combustion train as used by Stetser and Norton is shown in Fig. 6. *A* and *B* are 8-liter aspirator bottles. *B* is filled with oxygen through the reducing valve *N*; the upper bottle is graduated for each 250 c.c. The pressure of the water in *A* forces the gas into the furnace and the volume of oxygen used is measured by the fall of the water in *A*. *C* is a glass stop-

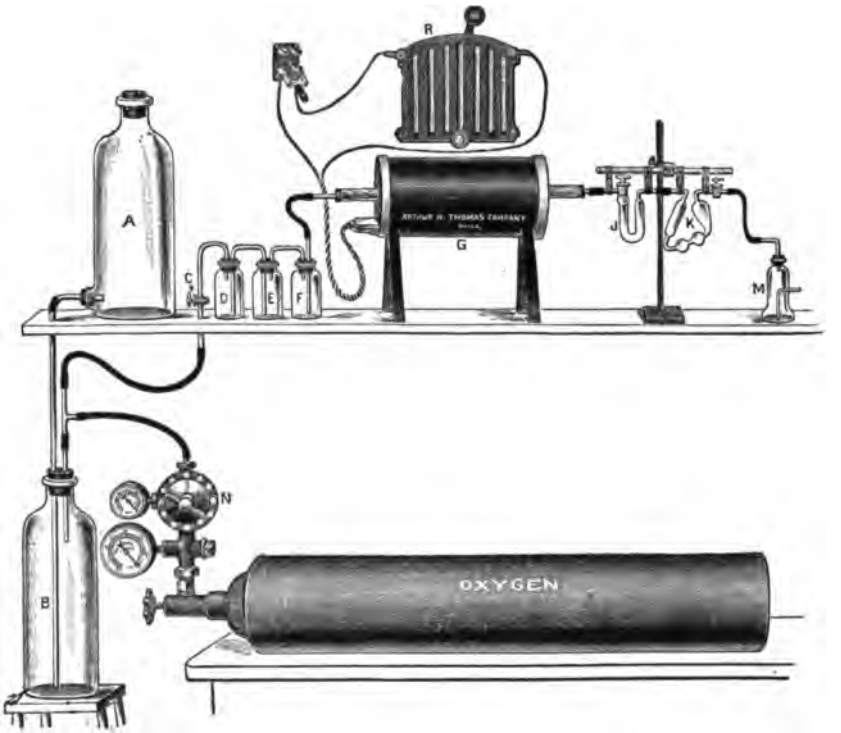

FIG. 6.

cock to be closed when filling *B* with oxygen. *D* is an empty safety bottle. Bottle *E* is one-third full of concentrated sulfuric acid and *F* contains ascarite (sodium hydroxide and asbestos). *J* contains 80-mesh zinc and *K* contains a little concentrated sulfuric acid.

Procedure.—First, test the apparatus to see that it does not leak; with *C* open and the stopcock on *K* closed, the pressure from *A* should not cause gas to bubble through *E* and *K* after a

few minutes. Then close *C* and slowly open the stopcock on *K*. Fill *B* with water, open the gas regulator valve, at *N*, and force the water from *B* into *A*. When bottle *A* is filled, close the regulator and the train is ready for the combustion. The exit end of the combustion tube, should be packed with some asbestos which has been heated to 1,000° in a current of oxygen prior to using.

Weigh out 1.36 g. of steel[1] into the alundum boat and introduce it into the hot furnace as in Method 1. Open the stop cock *C* and allow oxygen to pass through the apparatus; the sample should begin to burn in about 20 sec. If the sample is coarse or the temperature below 1,000°C., the combustion may be delayed. About 500 c.c. of gas should be allowed for the combustion of the steel and an equal volume to sweep out the carbon dioxide into the absorbing bulb. When, therefore, about 1 liter of oxygen has passed through the apparatus, the bulb is ready to be weighed. The time at which the sample begins to burn is indicated by the increased rate of flow through the liquid in *E*; a similar decrease marks the end of the combustion.

Standardization of the Stetser and Norton Absorption Bulb.—A freshly filled bulb should be run on the train for an hour and then weighed. It is not necessary to run the gas at a rapid rate during this time. The bulb is again attached and 2 more liters of gas are run through at the usual rate. The bulb should show neither gain nor loss. Should it do so, gas must be run through for another period of an hour. The bulb is then checked with 2 liters of gas. It should not, however, be necessary to run the bulb a second time.

When the bulb has reached a constant weight, the train may

[1] The directions are based on the paper of STETSER and NORTON, *Iron Age*, **102**, No. 8. They have reported the results of a carbon determination within 6 min. of the time the sample entered the laboratory. This includes the times spent in drilling the sample and in making the weighings. Since carbon dioxide contains 27.27 per cent of carbon and the per cent of carbon in a sample of steel weighing *s* g., and yielding *p* g. of carbon dioxide is $\frac{27.27 \times p}{s}$ it is clear that when 1.363 g. of steel is taken for analysis, $\frac{27.27 \times p}{1.363}$ $= 20\ p$. In other words, multiplying the weight of carbon dioxide by 2 and moving the decimal point 1 place to the right gives the per cent of carbon. In this case, the steel should be only weighed to the nearest centigram and the absorption bulb to the nearest half milligram.

be checked by running a government standard.[1] A fresh bulb may show slightly low results on the first three analyses. When filled with ascarite, one bulb will absorb from 10 to 15 g. of carbon dioxide without refilling.

3. DETERMINATION OF CARBON BY THE CORLEIS METHOD[2]

Principle.—Iron and steel samples of suitable fineness are dissolved by boiling with a mixture of chromic and sulfuric acids, which causes the oxidation of nearly all the carbon to carbon dioxide. A little of the carbon is usually set free as carbon monoxide or as hydrocarbon unless certain precautions are taken. Corleis found that the formation of such carbon compounds is greatly reduced by the addition of copper sulfate solution, but it is always best to heat the gases mixed with air in order to be certain that all the carbon is in the form of carbon dioxide. The carbon dioxide formed is absorbed by soda-lime contained in a U-tube or by caustic potash solution in a Geissler bulb. From the gain in weight, the amount of carbon in the sample is calculated.

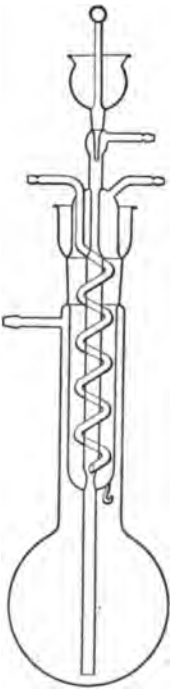

FIG. 7.

Apparatus and Necessary Solutions.—For combustion with chrome-sulfuric acid, the Corleis flask *K* with condenser is used (Fig. 7). There is a ground-glass connection between the condenser and the flask.

To keep the flask from breaking when it is heated, either support it on wire gauze or cover the bottom with asbestos paper as shown in Fig. 8. In the latter case, cut out suitably shaped pieces of asbestos paper (about 0.5 mm. thick), wet them with water, stick them to the bottom of the flask, and allow them to dry a little while in a drying closet at 110°.

The arrangement of the entire apparatus is shown in Fig. 8. Air is passed through the apparatus either by applying suction

[1] Carefully analyzed samples of various kinds of steel can be obtained from the Bureau of Standards at Washington, D. C.

[2] *Stahl u. Eisen*, **14**, 381 (1894).

at W or from a gasometer leading to W_1. To purify the air, place concentrated caustic potash solution (1:1) in the wash bottles W_1 and W_2 and soda-lime in the U-tube, U. Instead of these three tubes, a single soda-lime tower, with concentrated caustic potash solution at the bottom may be used.[1]

The gases from the combustion flask pass first through a small wash bottle, S, containing concentrated sulfuric acid. The glass tubing through which the gas enters should not dip into the sulfuric acid, but should end a few millimeters above the surface of the liquid. This flask has the function of holding back water vapor and sulfuric acid fumes from the boiling solution, without any danger of retaining appreciable quantities of the hydrocarbons in the sulfuric acid.

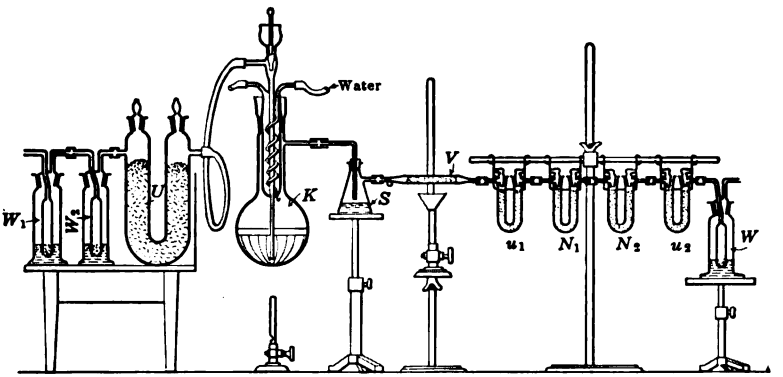

FIG. 8.

To S, attach a small combustion tube, V, made of difficultly fusible glass or of porcelain and containing copper oxide or platinized asbestos.[2]

If a glass tube is used, wrap it in iron gauze to prevent it from breaking when heated. The purpose of this combustion tube is to convert traces of carbon monoxide, or of hydrocarbons, into carbon dioxide.

The use of copper sulfate in the oxidizing liquid, however,

[1] *cf.* TREADWELL-HALL, "Text-book of Analytical Chemistry," Vol. II.

[2] The platinum capillary combustion tubes so frequently recommended have not given satisfaction; on continued use the platinum crystallizes and becomes permeable to gases.

prevents the loss of more than 2 per cent of the total amount of carbon present in any sample of ordinary iron or steel. In commercial work, therefore, this combustion tube may be omitted. Moreover, results obtained in test analyses with pure sodium oxalate show that the tendency of the method is to give results that are slightly high, which is another reason why this combustion tube may be omitted. In that case, connect the flask *K* directly with a small tube containing solid chromic-acid anhydride, between plugs of glass wool, and from this lead the gas into a U-tube containing a few glass beads wet with concentrated sulfuric acid. Place a little glass wool in each arm of this U-tube to break up any bubbles of sulfuric acid that may form during the analysis. Then, with the omission of *S* and of *V*, the arrangement is the same as shown in the drawing.

The last traces of moisture must be removed from the gases before the carbon dioxide is absorbed. This is accomplished by means of the small U-tube, u_1, containing calcium chloride or phosphorus pentoxide between plugs of cotton wool.

From this drying tube, the gases pass into the weighed soda-lime tubes N_1 and N_2, in which the carbon dioxide is absorbed. Usually all of the carbon dioxide is absorbed in the first tube. If the second tube begins to gain in weight, it is a sign that the first tube is nearly exhausted. When this happens, refill the first tube and then use it as the second tube in the train.

When carbon dioxide reacts with soda-lime, water is set free. To prevent the loss of this moisture, each tube must contain a little calcium chloride or phosphorus pentoxide. Fill the arm through which the gas enters with small pieces of soda-lime and fill half of the other arm with soda-lime. Then cover the soda-lime with a small piece of glass wool and fill up the tube with dry calcium chloride (or phosphorus pentoxide). In the top of each arm of the U-tube, place a plug of cotton wool. The kernels of soda-lime and of drying agent should be from 1 to 1.5 mm. in diameter; if much powder is present, it must be sifted out to avoid stopping up the tube. Too large lumps of either soda-lime or drying agent must not be used and the tubes must be filled tightly, or some gas may escape that should be absorbed.

As an added precaution, the second soda-lime tube is connected

with a calcium chloride (or phosphorus pentoxide tube) u_2 and this in turn is connected with a safety wash bottle, W, containing concentrated caustic potash solution; there is then no chance of water vapor or carbon dioxide being drawn back into the weighed tubes from the atmosphere. The wash bottle, W, also serves to indicate the rate at which the gas is passing through the apparatus.

Connections between the different parts of the apparatus are made by rubber tubing. In setting up the apparatus, take care that all the connections to the right of the Corleis flask are tight (glass on glass); in no case should the ends of the glass tubing be separated by empty sections of rubber tubing.

The following solutions are necessary:

(*a*) *Chromic Acid Solution.*—Dissolve 720 g. of chromic acid anhydride, which need not be chemically pure but should be practically free from organic matter, in 700 c.c. of water.

(*b*) *Copper Sulfate Solution.*—Dissolve 400 g. of copper sulfate crystals in water and dilute the solution to 2 liters.

Preliminary Boiling of the Chrome-sulfuric Acid Solution.—Remove the condenser from the flask K, and introduce 35 c.c. of the chromic-acid solution (*a*), 150 c.c. of the copper sulfate solution (*b*) and 200 c.c. of concentrated sulfuric acid (d. 1.84).

Replace the condenser and start a stream of water running through it. Boil the mixture in the flask to remove any organic matter which may be present, with the soda-lime tubes disconnected from the flask. While the solution is boiling, pass a slow stream of purified air through the apparatus and heat the small combustion tube V. Boil the solution for at least an hour in order to be sure that in subsequent work no carbon dioxide, or other gases absorbed by soda-lime, will be generated from carbon in the reagents. Then remove the flame and allow the apparatus to cool in a current of air.

Before starting an analysis it is advisable to run a blank on the apparatus, to find out how much the soda-lime tubes change in weight without the introduction of any substance to be analyzed.

Blank Run.—Rub the soda-lime tubes with a piece of chamois or a clean linen cloth, allow them to stand in the balance case for at least half an hour, then open the stopcocks for an instant to equalize the pressure and weigh them accurately to 0.0002 g.

Connect the weighed tubes to the rest of the train, open the stopcocks and pass a slow stream of air free from carbon dioxide through the apparatus. Boil the contents of the Corleis flask and heat the combustion tube for 2 or 3 hr. (the usual length of time for a combustion). Then remove the soda-lime tubes, close the stopcocks and place the tubes in the balance case. Remove the flame from beneath the Corleis flask and weigh the tubes, under the same conditions as before, after they have remained at least ½ hr. in the balance case.

If much more than 0.001 g. gain in weight is found in the blank determination, something is wrong. Besides possible impurities in the chromic acid, it may be that small particles of soda-lime or of drying agent have lodged in the glass tubing beyond the stopcocks, either due to a too rapid passage of the air current or to faulty filling of the tubes. In such a case the tubes would gain in weight constantly if left in the air, owing to absorption of carbon dioxide or of water. Care should be taken, therefore, to see that the tubing is free from soda-lime or drying agent. If necessary, the inside of the tubes may be wiped clean with small rolls of filter paper.

Slight gains in weight in the absorption tubes, which are almost always observed in the blank, should be allowed for in the determination.

Procedure.—While the acid solution in the flask is cooling, weigh the soda-lime tubes as previously described and also the sample of iron or steel, the carbon content of which is to be determined.

The weight of sample taken for analysis should be determined by its probable carbon content. Of cast iron, with 3 per cent or more of carbon, take 1 g.; of steel with 0.3 per cent or more take 3 g.; and of mild steel or wrought iron take 5 g.[1] Weigh the

[1] In weighing out samples it is a waste of time to weigh accurately to decimal places beyond those which affect the analysis. In the determination of carbon in steel, the absolute accuracy is determined largely by the degree of accuracy to which the soda-lime tubes, used for absorbing the carbon dioxide, can be weighed. Unless particular precautions are taken, such as reducing the weighings to vacuum, etc., the difference between the weights of the soda-lime tubes before and after the analysis cannot be assumed to be nearer than 0.001 g. to the truth. As a general rule, the next to the last significant figure in any value should not vary by more than one or

sample into a porcelain crucible, a glass-stoppered weighing tube, or, if it can be obtained in powder form (*e.g.*, gray cast iron), into a small glass basket which can be suspended, by means of fine platinum wire, from the hook which is usually provided on the end of the condenser, so that the sample is immersed in the liquid in the flask.[1] After the chrome-sulfuric acid solution has cooled sufficiently, connect the soda-lime tubes with the apparatus and pour a little sulfuric acid into the funnel at the top of the condenser to act as a seal; then test the entire apparatus to see if it is tight. To do this, close all the stopcocks in the absorption train and open the cock at the air supply to the Corleis flask. After a short time no more bubbles should pass through the Corleis flask. If bubbles do form, a leak is indicated between the Corleis flask and the calcium chloride tube u_1. When this section is found to be tight, open the first stopcock in the calcium chloride (or phosphorus pentoxide) tube; if after waiting a short time the current of air through the Corleis flask again stops, open

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two units. According to this rule, therefore, the soda-lime tubes should be weighed as carefully as possible to four decimal places, which is possible with the usual analytical balance. In the case of a sample of steel with 1 per cent carbon, a 3-g. sample will yield 0.110 g. of carbon dioxide and an error of 0.001 g. in this weight will correspond to 0.01 per cent carbon, or to one-hundredth of the entire carbon content. This precision is satisfactory here. An error of 0.03 g. in the original weight would correspond to the same fractional error. If, therefore, the original sample is weighed to the nearest centigram, any error introduced by neglecting the following decimal places will not have an appreciable effect upon the final result and any balance accurate to 0.01 g. can be used for weighing out the sample. It is not only a waste of time, but unscientific in principle, to determine values smaller than those which have a noticeable effect upon the result.

In weighing out smaller samples it is usually necessary to weigh more accurately but with cast iron the sample is rarely perfectly homogeneous so that in carbon determinations even with a 1-g. sample, it is sufficient if the original weighing is accurate to 0.01 g.

[1] For obtaining representative samples and for the method of weighing small samples for analysis the precautions mentioned in Part II of the book should be taken.

The shavings for the combustion with chrome-sulfuric acid treatment should not be more than 1 mm. thick if the combustion is to be finished in 2 or 3 hr. Thicker pieces should be hammered, broken or rolled before cutting. Hard-drawn wire or high-silicon tungsten steel often requires 3 or 4 hr. for combustion even if it is finely divided.

the next stopcock and so on up to the last stopcock on the final calcium chloride tube u_2. After the apparatus has been shown to be tight[1] and the air supply has been shut off, slowly open the last stopcock so that the excess of air will escape from the apparatus without rushing. A sudden rush of air might carry calcium chloride (or phosphorus pentoxide) dust either into or out of the weighed tubes, in each case causing a change in weight.

When the excess of air has escaped, remove the condenser and pour the weighed sample into the flask, or, if the sample has been weighed into a small glass basket, hang this on the hook. Replace the condenser at once and pour a little strong sulfuric acid over the connection between the condenser and the flask to make a tight joint. Raise the condenser again, just a trifle, so that a little of the sulfuric acid can run into the flask to wash down any particles of the sample which may have stuck to the glass.

Now light the gas under the combustion tube V and cause a slow stream of air, free from carbon dioxide, to pass slowly through the apparatus. Heat the Corleis flask, slowly at first, until the acid boils.[2]

Continue the boiling for about 3 hr., which is usually long enough to insure the complete solution and oxidation of the sample, unless it was in too coarse a condition. During this time the apparatus should be watched to see that the acid does not boil too violently, and that the air is run at the proper rate, not more than three bubbles a second. At the start if the contents of the flask are heated too quickly, particularly just before the solution boils, there is some danger of liquid sucking back toward the purification train. This is prevented by lowering the flame and increasing the speed of the air current. If, by accident, some of the liquid gets back into the tube U, the determination is

[1] If, instead of using an air reservoir in the experiment, suction is applied at the other end of the train, the manner of testing for leaks is the reverse. Gentle suction should be used in making the test and care should be taken not to let the air in too rapidly after the test.

[2] The current of air must be started as soon as the sample has been introduced. As the cold chromic-acid mixture has slight oxidizing power it is possible for small amounts of hydrogen and hydrocarbons to form. If these gases are not diluted and removed by the air current, they form mixtures with the air in the apparatus which, at certain concentrations of hydrogen and hydrocarbon, may explode in the combustion tube.

spoiled. During the last 15 min. of the boiling, it is well to increase the rate at which the air is passing so that it will drive over the last traces of carbon dioxide into the absorption train.

When the combustion is complete, stop the current of air and turn out the gas flames. Close the stopcocks of all the U-tubes that are in front of the flask and remove the soda-lime tubes. Allow these tubes to stand in the balance case for at least ½ hr. and weigh them with the usual precautions.

When the contents of the Corleis flask have cooled, remove the condenser and observe carefully whether there is any undissolved sample in the bottom of the flask. In case of doubt, this can be seen easily by pouring the contents of the flask into a large beaker containing considerable water. In most cases this is unnecessary and the solution may be used again for another determination. The quantities of reagents used are sufficient for the combustion of at least 10 g. of steel.

If some undissolved material should be noticed in the bottom of the flask, it is necessary on repeating the experiment to use finer material or to continue the boiling for a longer period. In no case, however, is it permissible to sift a sample of cast iron because the fine powder is likely to contain more graphite than the larger particles. Some kinds of iron alloys will not dissolve in the acid; the carbon in such alloys should not be determined by this method.

Computation.—If p represents the gain in weight of the soda-lime tube (or tubes) in the analysis of a sample weighing s g., then

$$\text{Per cent C} = \frac{27.3 \times p}{s}$$

Accuracy of the Values found by the Chrome-sulfuric Acid Method

Allowing for differences in the composition of the samples, as discussed in Part II of this book, the errors which may occur in the chrome-sulfuric acid method are traceable chiefly to errors in weighing and to the gain in weight of the soda-lime tube from some source other than the carbon in the sample.

Assuming that the errors of weighing are not greater than ±0.001 g. and that the first soda-lime tube has an average weight

of 0.002 g. too high the total error in a properly conducted analysis probably lies between +0.001 to +0.003 g. carbon dioxide.

The error in all cases would be found in the second decimal place of the calculated percentage and would be, for example, between 0.01 and 0.03 per cent with a 3-g. sample or between 0.005 and 0.02 per cent with a 5-g. sample.

It follows from this that the carbon content is uncertain in the second decimal and it is sometimes customary, for this reason, to write the second figure small.

The use of a third decimal, except in such cases where very unusual precautions have been taken, is not only unnecessary but also shows that the analyst is ignorant of the probable error of the method.

If the carbon determination is carefully carried out, the following values may be taken as permissible variations in the analysis of samples weighing about 3 g.

With a carbon content from	to	Greatest allowable deviation
0.02	0.15 per cent	± 0.005 per cent
0.15	1.00 per cent	± 0.010 per cent
1.00	2.00 per cent	± 0.020 per cent
2.00 and higher per cent		± 0.030 per cent

Greater accuracy, as for example, that given by Bischoff[1] for low carbon material, can scarcely be attained.

Applicability of the Chrome-sulfuric Acid Process

The chrome-sulfuric acid method is suitable for all sorts of irons, steels and special steels as well as for numerous other metals and alloys used in the steel industry. The following substances can be decomposed without leaving a residue; ferro-manganese, chrome-manganese, ferro-vanadium, ferro-molybdenum, ferro-titanium, manganese-titanium, ferro-boron, metallic nickel and metallic molybdenum in the form of fine powder. The method cannot be used for the following materials which are scarcely attacked after 4 hr. treatment; ferro-silicon, ferro-tungsten, metallic tungsten, ferro-phosphorus, ferro-chromium, and metallic molybdenum either as wire or as sheet.

[1] *Stahl u. Eisen*, **22**, 727.

4. DETERMINATION OF TOTAL CARBON BY THE POTASSIUM-CUPRIC-CHLORIDE METHOD

This method, for a long time considered better than a direct combustion, does not give reliable results with certain alloy steels, especially chrome-tungsten steel, probably on account of some carbon being lost as hydrocarbon. It will give reliable results with all ordinary samples of iron and steel.

After the removal of the iron, the carbon can be determined by combustion either in an electric or gas-heated furnace. Inasmuch as many laboratories are not equipped with electric furnaces, especially those laboratories which use the double chloride method, the procedure will be described as carried out with a gas-heated furnace.

Principle.—When metallic iron is placed in contact with a solution of a cupric salt, the iron, because of its greater solution tension replaces the copper which is precipitated upon the remaining iron. In the presence of an excess of cupric salt, the deposited copper reacts to form cuprous chloride which is kept in solution by the potassium chloride, and to some extent by the hydrochloric acid, with which it forms a soluble double salt. The reactions may be expressed as follows:

$$Fe + CuCl_2 = FeCl_2 + Cu$$
$$Cu + 2CuCl_2 = Cu_2Cl_2$$

or

$$Fe + Cu^{++} = Fe^{++} + Cu$$
$$Cu + Cu^{++} = 2Cu^{+}$$

Since hydrochloric acid reacts with iron carbide and with its solid solution in iron, setting free gaseous hydrocarbons, it was at first thought necessary to carry out the treatment with potassium cupric chloride in a perfectly neutral solution but it was found later that no hydrocarbons were set free by dilute hydrochloric acid in the presence of a cupric salt and that, in fact, the presence of nearly 10 per cent by volume of strong hydrochloric acid is not only permissible but beneficial; in many cases the results are higher and nearer the truth.

Necessary Apparatus and Solutions.—The combustion train, Fig. 9, consists first of a short preheating furnace containing

a glazed porcelain tube filled with granular cupric oxide between loose plugs of ignited asbestos. This serves to oxidize any gaseous carbon compounds that may possibly be present in the oxygen supply. Between this furnace, and the longer, ten-burner combustion furnace in which the sample is burned, is a Geissler bulb, with the bottom bulbs about two-thirds filled with strong caustic potash solution (1 : 1). This serves to remove any carbon dioxide from the oxygen, or air, used in the combustion.

The combustion tube, made of glazed porcelain, contains copper oxide in the end near the absorption train, between plugs of ignited asbestos, but space is left at the other end so that the sample can be introduced into the hottest part of the furnace.

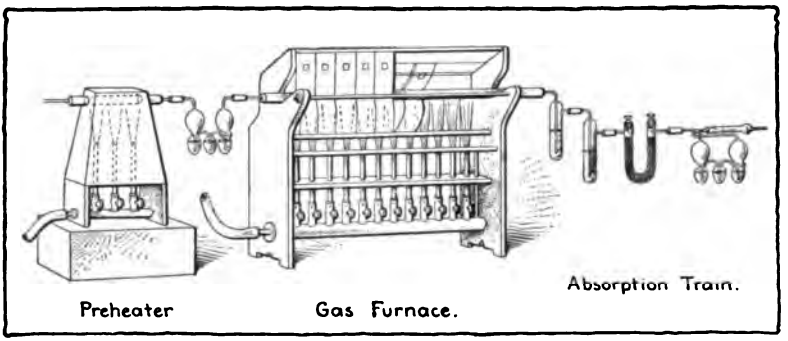

FIG. 9.

The absorption train consists of a small bubble tube about one-fourth filled with a saturated solution of ferrous sulfate (60 g. $FeSO_4.7H_2O$ in 100 c.c. water), a similar tube containing about 10 c.c. of a saturated solution of silver sulfate in sulfuric acid (d. 1.40), a U-tube containing granular calcium chloride (or phosphorus pentoxide) and a Geissler bulb containing caustic potash solution (1 : 2) with a prolong filled with calcium chloride.

The purpose of the ferrous sulfate is to reduce any chlorine that may be evolved during the combustion of the residue obtained after treatment with potassium-cupric-chloride solution. The ferrous sulfate changes the chlorine to hydrochloric acid which is retained partly as ferric salt; if any escapes it is caught by the silver sulfate in the next tube.

In filling the calcium chloride tubes, especially the prolong of

the Geissler bulb, take care to press down the granular calcium chloride, using particles ⅛ in. in diameter. If the tube is loosely filled some moisture is likely to escape; for this reason a negative blank is often obtained by the beginner.

Instead of the tubes of ferrous sulfate and silver sulfate, the use of anhydrous cupric sulfate followed by anhydrous cuprous chloride has been recommended, or, as suggested by E. S. Johnson, a column of 20-mesh zinc between glass-wool plugs will serve to remove either acid or chlorine.

Instead of the Geissler tube, U-tubes filled with soda-lime and calcium chloride may be used as in Method 3, p. 23.

Potassium-cupric-chloride Solution.—Dissolve 300 g. of the double chloride in water containing 75 c.c. of concentrated hydrochloric acid (d. 1.2), and dilute the solution to 1 liter.

Ignited Asbestos.—Place the asbestos in a dish and heat it to bright redness in a muffle furnace. Remove the dish, allow the asbestos to cool somewhat, and turn over the asbestos. Again heat to redness in the muffle furnace. While cooling, keep the dish covered to prevent dirt from falling into it. If necessary, cut the ignited asbestos into short pieces and add enough water to form a fairly thick suspension.

Procedure.—Weigh out 3 g. of ordinary steel, or 1 g. of pig iron, into a 400-c.c. beaker and cover the sample with 100 c.c. of the double chloride solution for each grain of metal taken. Stir the solution with some form of mechanical stirrer until all the iron has dissolved. It is very easy to tell when the solution is complete by holding the beaker up to the light. If pieces of undissolved metal remain, they will be coated with metallic copper, which is readily distinguished from the black carbonaceous residue.

Prepare an asbestos filter by placing a coil of fairly heavy copper wire in the bottom of a tube funnel, like that shown in Fig. 2, at C, and cover this coil with about an inch of wet, ignited asbestos. Filter off the residue from the double chloride treatment and wash out the beaker with 10 c.c. of double chloride solution diluted with an equal volume of water. Moderate suction may be used but this is not necessary. Transfer all of the residue to the filter by means of dilute hydrochloric acid from a wash bottle. Finally wash the residue on the filter with hot

water until free from chloride. Carefully push up the filter from the funnel and transfer it, bottom down, to a clean watch-glass. Rub the side of the funnel with ignited asbestos to remove any adhering carbon, and add this to the main portion on the watch-glass. Cover and dry for an hour or two at a temperature between 95 and 100°. It is then ready for the combustion.

In starting with a freshly filled combustion tube, it should be heated ½ hr. while passing a current of oxygen through it. Then attach the absorption tube, weighed with the same precautions as described for weighing the soda-lime tubes in Method 3, p. 26, and make a blank run to be sure the apparatus is ready for use. Heat the tube red hot and pass oxygen through it for 20 min., at a rate such that two or three bubbles per second pass through the absorption tube, then turn out the burners under the back end of the furnace, where the sample is to be introduced, and pass air through the tube for another 20 min. This may be done either by having an air reservoir under pressure or by applying suction at the front end of the furnace. A simple way of getting suction is to have two large bottles, one on the working bench and the other on the floor. By filling the upper bottle with water and allowing it to siphon slowly into the lower bottle, sufficient suction is obtained. In this way the volume of air passed through the combustion apparatus is shown.

If after the blank run, the absorption tube does not show over 0.0010 g. change in weight, the apparatus is ready for use.

Push the dried asbestos well into the back end of the furnace and wipe out the watch-glass with dry, ignited asbestos. Make sure that the carbon reaches far enough into the tube to get the full heat of the furnace. If the combustion tube is cold, light the preheating furnace and turn on the oxygen, allowing it to pass through the absorption bulb at a maximum rate of three bubbles a second. Light the two forward burners under the combustion tube and gradually turn up the flames until this end of the furnace tube is red hot. Then light the next burner and continue in this way until finally the whole furnace is hot.

To avoid burning the rubber stoppers at the ends of the combustion tube, place shields of heavy asbestos board around each end of the tube where it projects from the furnace and wrap

each end near the stopper with a narrow band made of several thicknesses of cheese cloth with the ends dipping in cold water.

After 20 min. have elapsed from the time the last burner was lighted, stop the current of oxygen and pass a current of air through the tube at the same rate to sweep out all of the carbon dioxide. Gradually turn down the burners under the tube, but if it is to be used immediately for another combustion, it is best to keep the front end hot. Finally detach the Geissler bulb and weigh with the usual precautions.

NOTES.—Instead of oxidizing the residue from the double chloride treatment by a dry combustion, many chemists prefer to oxidize it in the wet way by means of chrome-sulfuric acid, as in Method 3, p. 23.

Instead of a combustion tube, the Gooch tubulated crucible or the Shimer crucible may be used. When the combustion is carried out in a crucible, place after the crucible a copper tube about 10 in. long and 5/16 in. inside diameter, with its ends cooled by water jackets. In the center of this tube place a disk of platinum gauze and a 3-in. roll of silver foil, on the side near the crucible, and copper oxide on the other side. Plug the ends of this tube with glass wool and heat it with a burner which is fitted with a flame spreader.

Test Analyses.—To illustrate the accuracy of the above method, the following values are taken quite at random from certificates issued by the Bureau of Standards at Washington, D. C. At the present time most of the analyses made at the Bureau itself are by a direct combustion method.

A sample of pig iron was analyzed by the direct combustion method by five different chemists and the average value obtained was 2.464 per cent carbon; eight chemists obtained an average value of 2.461 per cent carbon by the solution and combustion method.

In a sample of Bessemer steel, nine chemists obtained the value 0.805 per cent carbon by direct combustion and three chemists obtained an average value of 0.806 per cent carbon by solution and combustion.

With a sample of vanadium steel, eight chemists obtained an average value of 0.348 per cent by direct combustion and five chemists obtained an average value of 0.348 per cent carbon by solution and combustion.

With a sample of nickel steel, seven chemists obtained an average value of 0.375 per cent carbon by direct combustion and

five chemists obtained the average value of 0.379 by solution and combustion.

4. DETERMINATION OF CARBON BY THE DEISS METHOD

The first method described for the determination of carbon was worked out in the laboratories of the Bureau of Standards at Washington, D. C. The following method was recommended by E. Deiss when working at the Royal Testing Bureau near Berlin. The principle of the method is the same as the method of Cain and Maxwell except that soda-lime is used to absorb the carbon dioxide and the gain in weight of the absorption tube is determined. When soda-lime of suitable physical and chemical properties is available it is thoroughly satisfactory as an absorbent.

Apparatus.—*Principle.*—On heating iron and steel to about 1,100 or 1,200° in a current of oxygen, the metal is oxidized completely to ferroso-ferric oxide and any other elements that may be present are also changed to oxides. Of these latter elements carbon and sulfur form volatile compounds which can be absorbed and determined. With excess of oxygen, carbon forms carbon dioxide and sulfur, either the dioxide or the trioxide.

If the evolved gases were absorbed directly in a soda-lime tube and the carbon content calculated from the gain in weight, the results might be too high, due to the sulfur present, or too low because of insufficient oxidation (formation of carbon monoxide).

In order to determine carbon accurately, therefore, the gases must be freed from oxides of sulfur by suitable means and any carbon monoxide must be oxidized to dioxide before the absorption train is reached.

Apparatus.—For heating the porcelain or quartz tube in which the combustion takes place, a horizontal tube furnace with variable resistances and connection with a high-tension electric circuit is desirable.

If many carbon determinations are to be made a tube furnace of large diameter is recommended; several porcelain tubes can be heated in it at the same time and with the use of only a little more current. A platinum, platinum-rhodium thermoelement with a millivoltmeter is used to measure the temperature[1] in the furnace.

[1] For further details consult LE CHATELIER'S "High-temperature Measurements" (Boudouard-Burgess).

To avoid overloading the furnace at the beginning of the heating it is best to have an ammeter in the circuit.

The combustion itself takes place in a tube made of quartz or glazed porcelain. The tube contains a little coarse copper oxide and some chromate mixture. To prepare the latter, mix together 9 parts of potassium chromate with 1 part of potassium dichromate, heat till sintered in a porcelain crucible and grind the sintered mass to a coarse powder. This charge would at once melt and lose its efficiency if placed in the hottest part of the tube; in the part that projects from the furnace it is heated by radiation sufficiently to effect the conversion of any carbon monoxide to dioxide and of any sulfur dioxide to sulfuric acid anhydride which is retained by the chromate mixture.

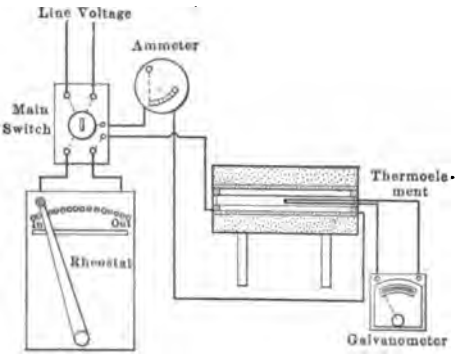

FIG. 10.

Place a loose plug of ignited asbestos just at the end of the part of the tube that is inside the furnace, after this a layer of copper oxide about 2 cm. long and then an equally long layer of chromate mixture, also between asbestos plugs. The copper oxide is less fusible than the chromate mixture. If, however, it reaches the hot part of the tube and melts, the tube is likely to crack on cooling.

A sketch showing the connections for the tube furnace and for the thermoelement is given in Fig. 10

The arrangement of the entire apparatus is shown in Fig. 11. Its different parts will be described in succession and in the direction of the current of oxygen.

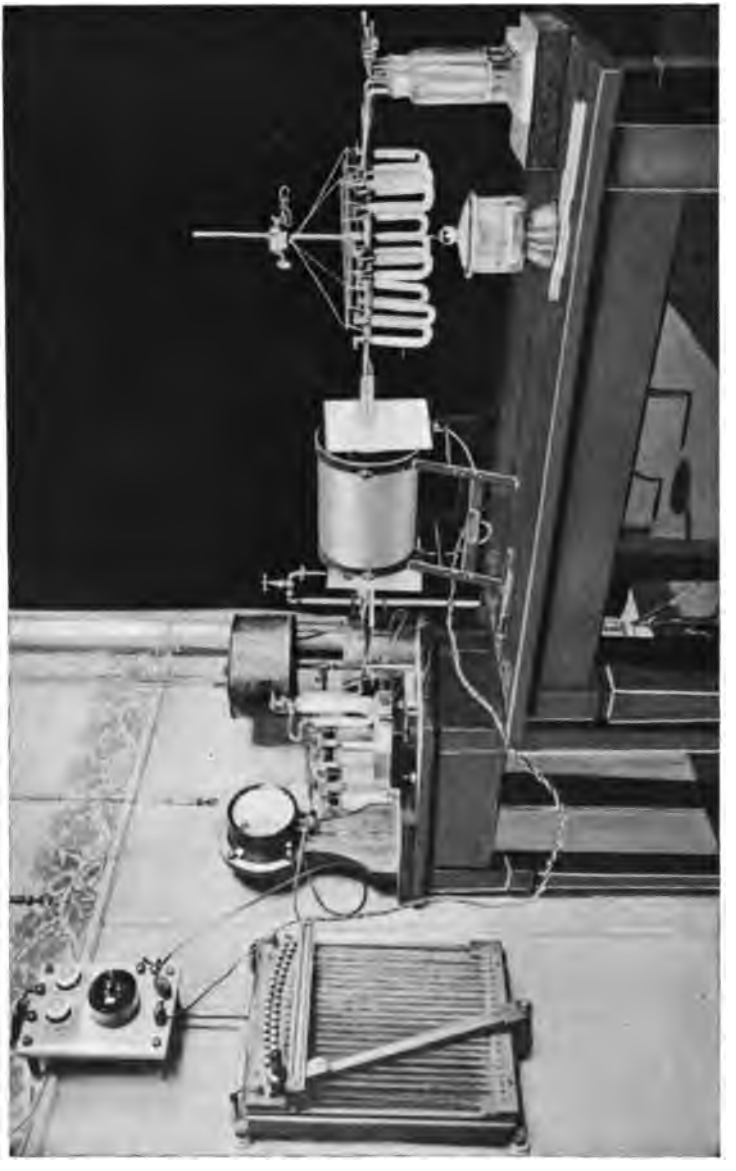

FIG. 11.—Apparatus for carbon determination with an electric furnace.

The oxygen is kept in a gasometer filled from a tank of compressed gas. In order to purify the oxygen from the gasometer it is passed first through several wash bottles containing concentrated caustic potash solution (1 :1) then through a large soda-lime tube and finally through a tube containing calcium chloride (or phosphorus pentoxide). A piece of rubber tubing closed with a pinchcock leads from the last drying-tube to the combustion tube or, in case several tubes are used in one furnace, this rubber tubing leads to a forked glass tube and from there to the different porcelain tubes. The porcelain tubes and the thermoelement in its protecting tube are held firmly in the openings of the furnace with the aid of asbestos wool; take care that the tubes do not come in direct contact with one another or with the walls of the furnace. A good method of keeping the tubes apart is to use a thick piece of asbestos board with holes corresponding to the number of tubes used and through which the tubes will project from both ends of the furnace.

The thermoelement should extend far enough into the furnace so that its junction will be in the hottest part of the tube. The wires of the thermoelement are connected with the poles of the galvanometer and by closing the switch in the main circuit it is possible to tell whether the connections are correctly made. The pointer should move toward the scale. Place the porcelain tubes, filled with copper oxide and the chromate mixture, in the furnace with the filled parts at the front end, farthest away from the oxygen tank, so that the oxygen passes first through the empty part of the tube, in which the combustion boat is to be placed, then through the copper oxide and chromate mixture, and finally into the absorption train. The first tube in the train contains calcium chloride (or phosphorus pentoxide) to absorb moisture from the gases and the two tubes following are filled with soda-lime and calcium chloride (or phosphorus pentoxide) to absorb carbon dioxide. These tubes are filled and handled exactly as in the chrome-sulfuric acid method (p. 26). Attach a safety tube of concentrated sulfuric acid to the last soda-lime tube, to prevent any moisture from getting back into the tube in case the gases should suck back. This tube also serves to indicate the rate at which the gases are passing.

Porcelain tubes, glazed on the outside only, or quartz tubes,

may be used for the combustions. If the furnace is 30 cm. long, tubes of 50-cm. length are used. A furnace with an internal diameter of 50-mm. will hold a thermoelement and three combustion tubes of 12-mm. outside diameter.

The porcelain boats used in the combustion for holding the sample should preferably be of unglazed material. To avoid any possible fusing of the boat to the inner wall of the tube, even when boats glazed on the outside are used, it is a good plan to wind pieces of asbestos fiber around the boat about 1 cm. from each end. When the boat is introduced into the tubes these fibers prevent it from coming in direct contact with the tube walls.

Procedure.—After weighing the soda-lime tubes, using the precautions described in the chrome-sulfuric acid method, weigh the sample into a boat which has been previously wound with asbestos fibers and ignited. For iron and steel samples with high-carbon content, a weight of 1 g. is usually sufficient and this can be spread on a boat 7 cm. long, 8 mm. wide and 5 mm. deep. For weighing larger samples (2 or 3 g.) which are necessary with low-carbon material, boats about 13 cm. long, 7 mm. wide and 6 mm. deep should be used. Take care in filling the boat not to let pieces of the sample project over the edge, as the molten oxide formed during the combustion will then drop off and come in contact with the inside of the tube. The very coarse shavings which sometimes form in taking the sample cannot be used on this account and must be brought into a denser and flatter form by hammering in a diamond mortar.

It is best not to have the sample too fine. Fine shavings and powder burn very easily, to be sure, but the combustion starts so quickly and proceeds so rapidly that there is danger of there being an insufficient oxygen supply (formation of carbon monoxide) and there is also danger of the liquid in the last flask sucking back, unless the rate of flow of the oxygen is increased quickly. The combustion goes less violently but completely with coarse shavings or thick pieces. Pig iron chips, 2 mm. thick, will burn readily in the electric furnace, whereas pieces of the same size will be attacked scarcely at all by 4 hr. treatment with the chrome-sulfuric acid mixture.

While the soda-lime tubes and the sample are being weighed, pass a slow current of oxygen through the previously ignited

porcelain (or quartz) tube. Connect the closed soda-lime tubes in place, push the boat with the sample to the center of the tube by means of a suitably bent wire or a glass rod, stopper the tube and make a test to see if the apparatus is tight. For this purpose first open the stopcock next to the furnace and allow oxygen to pass into the apparatus until no more bubbles pass through the wash bottle from the gasometer. If the apparatus is found to be tight up to this point, open the next stopcocks in the tubes of the train, one by one, waiting each time until the gas bubbles stop. Then, if the connections are all tight, relieve the excess oxygen pressure by opening gradually the stopcock in the front end of the train. Continue passing a slow stream of oxygen through the apparatus and begin the heating.

In working with a Heraeus furnace of 50-mm. internal diameter, with which the maximum temperature of 1,300° is given with a current of 10.5 amperes at 220 volts, the method of operation is as follows:

First, have all the resistance in the electric circuit. Turn on the current and move the rheostat arm back until the ammeter shows 9 amperes. As the current drops 1 or 2 amperes cut out more resistance and keep the current at 9 to 10 amperes.

During a combustion the galvanometer indicates approximately these changes in temperature:

after 5 min.	200°C.
after 15 min.	650°C.
after 30 min.	850°C.
after 45 min.	980°C.
after 60 min	1,060°C.
after 67 min.	1,100°C.

The combustion usually starts at a temperature between 850 and 980° and is indicated by a sudden slowing up of the gas current in the last wash bottle and an increase in the rate at which the oxygen flows through the first wash bottle. To prevent the back pressure from forcing air into the soda-lime tubes, increase the supply of oxygen while the sample is burning.

Maintain the temperature of the furnace for 15 or 20 min. at 1,100° or, at the most, 1,200°, and continue passing a slow stream of oxygen through the apparatus.

At the end of this time the combustion is surely ended. Shut

off the electric current, turn the lever of the resistance box back and pass oxygen through the tube for 15 min. longer, to drive all of the carbon dioxide out of the combustion tube and drying tube. Finally, close the stopcocks of the soda-lime tubes, remove them from the train and weigh them after allowing them to stand at least half an hour in the balance case.[1] After the soda-lime tubes have been taken off, close the stopcock from the oxygen tank and allow the furnace to cool.

If another combustion is to be made at once, weigh out the new sample while the furnace is cooling. When the temperature has fallen to about 600° or less, pull out the old boat with a hook made of clean copper wire. Pass oxygen through the tube for 5 min., connect the weighed soda-lime tubes and push the new sample into the tube. Turn on the electric current and proceed as before. The time taken to bring the warm tube up to the combustion temperature is much less now and less current is used, two factors of great importance where work is being done on a large scale. If large pieces are used for combustion it often happens that the ferric oxide after the combustion is left in the form of loose pieces which can easily be removed from the boat; if the material is finely divided the mass usually fuses to the boat.

The porcelain boat can be cleaned for use a second time by heating it for a long time with concentrated hydrochloric acid to remove the adhering oxide. This hardly pays, however, when the price of unglazed procelain is low.

The computation of the carbon content is the same as in the previous method.

Accuracy of the Values Found by the Direct Combustion Method

The weight changes in the soda-lime tubes in the blank runs are within the error of weighing. Assuming the error of weighing to be not greater than ± 0.0005 g., the percentage errors are:

For a 1-g. sample ± 0.015 per cent
For a 2-g. sample ± 0.007 per cent

[1] This leaves oxygen in the tubes which weighs slightly more than the air they originally contained. The tubes are so small, and there is so little free air space that it is not necessary to correct for this slight error. If the initial weight of the tubes was made when they were filled with oxygen, this error disappears.

The method of direct combustion in oxygen is, therefore, slightly more exact than the chrome-sulfuric acid method. In this case, too, the errors are found in the second decimal place so that if small weight samples are taken (1 to 3 g.) the allowable deviations are the same as those given for the chrome-sulfuric acid method (p. 31).

In order to reduce the effect of the weighing error and so get more accurate carbon values, a larger sample may be taken (10 to 15 g.) and burned in a larger porcelain boat and in a large tube.

Applicability of the Method

All the metals and alloys mentioned under the chrome-sulfuric acid method, including those which could not be decomposed by that method, will be decomposed in a current of oxygen at temperatures between 1,100 to 1,200°.

With certain substances, like ferro-vanadium and molybdenum which give readily fusible oxides that are likely to injure the combustion tube, it is advisable to place the sample in the boat on top of some absorbent material such as ignited alumina.

DETERMINATION OF GRAPHITE AND TEMPER CARBON

Principle.—Graphite and temper carbon are so similar in their chemical behavior that they cannot be separated by analytical methods. The precipitation and separation of combined carbon is based on the fact that graphite and temper carbon are not attacked by boiling dilute nitric acid, while the various forms of combined carbon form volatile compounds, or compounds soluble in nitric acid.

Procedure (Ledebur).—With dark gray cast iron use 1 g., with light gray or tempered iron 2 to 5 g., and with high-nickel steel use 5 to 10 g. of the metal.[1] Weigh the sample into a 300 to 600-c.c. beaker and heat it with dilute nitric acid (d. 1.2) using about 25 c.c. of acid for each gram of metal. Immerse the beaker in cold water, or hold it under the tap, to prevent too

[1] In determining graphite or temper carbon it is often better to use small pieces rather than turnings. This is especially true when it is a question of determining the amount of graphite or temper carbon at one place on a specimen. (See Part II.)

violent action at the start with a consequent loss of material due to spattering. After the action has slackened, heat the beaker on a sand bath, or over an asbestos plate, until the metal is completely dissolved. If the sample contains much silicon (*e.g.*, gray pig iron) add ½ to 1 c.c. of hydrofluoric acid[1] to dissolve the gelatinous silicic acid, which would otherwise clog the pores of the filter. Take care not to let any particles of paraffin from the acid container drop into the solution. Cover the beaker with a watch-glass and boil the solution very gently, over a small flame, for 1 or 2 hr. Then dilute with water, set the beaker aside for a short time to allow the insoluble matter to settle, and filter through a well-fitting asbestos filter[2] into an Erlenmeyer flask.

After the liquid and residue have all been poured out of the beaker, rub the sides of the glass with a rubber-tipped stirring-rod to remove any adhering particles, then rinse the beaker with hot water and wash the filter and residue until free from acid.

The wet residue on the filter may be used at once if the carbon is to be determined by the Corleis method. Otherwise it should be dried at 110°, transferred to a combustion boat and analyzed by any of the methods that have been given for the determination of total carbon.

Instead of the Ledebur method, the following treatment is recommended by the American Society for Testing Materials.

Dissolve the sample in nitric acid, d. 1.13, and boil the solu-

[1] It is best to pour the hydrofluoric acid into the beaker in such a way that it will not come into immediate contact with the glass.

[2] Asbestos for this purpose is prepared as follows: Cut long-fibered asbestos into pieces about 1 cm. long and heat them with successive portions of strong hydrochloric acid, until a portion of fresh acid is not colored appreciably yellow. Wash the asbestos free from acid with hot water, dry the mat of asbestos in the hot closet and finally ignite it in a porcelain crucible to destroy any organic matter.

To make the filter, place some of the ignited asbestos in the stem of an ordinary short funnel. By a stream from the wash bottle, distribute the fibers in such a way that the fine material will close the pores made by the coarser fibers and form a tight mat.

The filter is known to be tight if the funnel stem will stay full of water. An asbestos filter made in this way will filter rapidly and if enough asbestos is used will be tight enough to hold all but the most finely divided precipitates. Another method of preparing ignited asbestos is given on page 34.

tion 5 or 10 min. to expel hydrocarbons. Filter the residue on ignited asbestos and wash several times with hot, dilute caustic potash solution, d. 1.10, then with dilute hydrochloric acid and finally with hot water. Dry at 110° and analyze as for total carbon.

Colorimetric Method for Determining Carbon in Steel

Principle.—This method, suitable only for routine work, depends upon the fact that the color produced by dissolving steel in nitric acid deepens as the carbon content increases. The color produced by free cementite varies somewhat from that produced by the same quantity of carbon present as martensite and on boiling the solution some of the carbon is expelled in the form of hydrocarbons. It is important, therefore, that the color should be compared with that produced by the same weight of an analyzed steel containing practically the same amount of carbon and with the carbon in the same metallographic condition. It is necessary to use a series of steels with varying carbon contents as standards. The standards must also be prepared at the same time under exactly the same conditions.

Procedure.—Dissolve 0.2 to 0.5 g. of steel in a test tube with 5 to 20 c.c. of nitric acid, d. 1.24, made by diluting 1,000 c.c. of concentrated acid, d. 1.42, with 1,200 c.c. of distilled water.[1] Boil gently until all the steel is dissolved. Cool and compare with standards prepared at the same time.

[1] The nitric acid is approximately 7-normal.

CHAPTER III

MANGANESE

The manganese content of iron and steel varies considerably. In ingot iron it is usually very low and in ordinary steel it rarely amounts to more than 1 per cent. In manganese steel and in certain other special steels, however, much more manganese is present. Certain grades of cast iron contain considerable manganese and in ferro-manganese, silico-manganese, chrome-manganese, and other manganese alloys, this element constitutes the most important constituent.

To the analytical chemist, manganese is an interesting element because there are so many characteristic reactions that may be used for its qualitative detection and quantitative determination. There are, for example, a number of manganese compounds easy to prepare which are so insoluble that they may be used for gravimetric methods. Then again, manganese compounds in various states of oxidation are known and favorite volumetric methods depend upon the oxidizing power of certain of these compounds. Manganese also forms highly colored compounds and one of these forms the basis of several colorimetric methods. Attempts have also been made to determine manganese electrolytically but it is rather difficult to maintain conditions such that only one electrolytic reaction will take place; it is easy to make permanganate electrolytically and easy to deposit manganese as dioxide upon the anode but it is difficult to make one of these oxidation reactions take place quantitatively without any of the other product being formed at the same time so that electrolytic methods for determining manganese are not to be recommended.

Personal preferences will always have a great deal to do with the choice of the method used for determining the manganese content of iron or steel and also with regard to the details of carrying out the method. No attempt will be made to describe all of the good methods but typical ones will be chosen.

For determining small quantities of manganese the most suitable methods are those which depend upon the formation of permanganate. This may be accomplished by the action of sodium bismuthate, ammonium persulfate in the presence of a catalyzer, or by lead dioxide. The violet color of permanganate can be obtained by any of the above reagents under suitable conditions when considerably less than 1 mg. of manganese is present in the solution. If the quantity of manganese is very small, a colorimetric method is suitable but with higher manganese content it is better to find out how much permanganate has been formed by discharging the color with a known quantity of a reducing agent such as ferrous salt or arsenite.

Other oxidizing agents convert bivalent manganous ions, formed by dissolving the metal in acid, into insoluble manganese dioxide. The precipitated dioxide may be analyzed gravimetrically or its oxidizing power upon a solution containing a known quantity of ferrous salt or oxalate may be determined. One of the well-known volumetric methods depends upon the fact that when bivalent manganese ions in nearly neutral solution are allowed to react with permanganate ions, all of the manganese, both of the sample and reagent, can be converted into insoluble manganese dioxide.

Gravimetrically, manganese may be determined accurately as pyrophosphate, $Mn_2P_2O_7$, as sulfate, $MnSO_4$, or as sulfide, MnS. Of these last compounds, the sulfate is soluble in water but salts of acids less volatile than sulfuric acid may be easily changed to sulfate in a weighed crucible or dish and the sulfate of manganese can be heated gently without undergoing decomposition.

All oxides of manganese are converted into Mn_3O_4 upon strong ignition, and manganese is often determined in this form.

The method first to be described is that recommended as standard by the American Society for Testing Materials. A. A. Blair[1] has characterized the method as more accurate than any other method known to him and Blum,[2] working at the Bureau of Standards, has shown that it can be used even with materials rich in manganese.

[1] *J. Am. Chem. Soc.*, **26**, 793 (1904).
[2] *Ibid.*, **34**, 1382 (1912).

1. DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD

Principle.—When sodium bismuthate is added to a cold solution of manganous salt, containing considerable free nitric acid and no chloride or reducing substance, the colorless manganous cations are converted into purple permanganate anions:

$$5BiO_3^- + 2Mn^+ + 14H^+ = 2MnO_4^- + 5Bi^{+++} + 7H_2O$$

The excess of the reagent is insoluble and can be removed by filtration through asbestos.

The permanganate ions on being treated with a known quantity of suitable reducing agent are changed back to manganous ions and the excess of reducing agent is determined usually by titration with standardized permanganate solution.

Schneider[1] originally proposed the use of bismuth tetroxide as oxidizing agent and titrated the permanganate with hydrogen peroxide solution. Reddrop and Ramage[2] used sodium bismuthate instead of the tetroxide, Bi_2O_4, and subsequently Ibbotson and Brearley[3] replaced the hydrogen peroxide with ferrous ammonium sulfate. To-day, in the steel laboratories of the United States, sodium arsenite is commonly used, partly because the solution is more stable; the end-point of the titration is less satisfactory than when a solution of a ferrous salt is used.[4]

The reaction between the permanganate and the various reducing agents may be expressed as follows:

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{++} + 8H_2O + 5O_2 \uparrow$$

$$MnO_4^- + 5Fe^{++} + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O$$

$$2MnO_4^- + 5HAsO_3^{--} + 6H^+ \rightleftarrows 2Mn^{++} + 5HAsO_4^{---} + 3H_2O$$

Reagents Required.—1. *Sodium Bismuthate.*—The product sold under this name is of more or less indefinite composition but corresponds fairly closely to the formula $NaBiO_3$. It may be prepared by heating 20 parts of caustic soda nearly to redness in an iron or nickel crucible, adding, in small quantities from time to time, 10 parts of dry, basic bismuth nitrate, followed by

[1] *Ding. poly., J.*, **269**, 224.
[2] *J. Chem. Soc.*, **67**, 268 (1895).
[3] *Chem. News*, **84**, 247 (1901).
[4] *cf.*. KÜHLING, *Ber.*, **34**, 404 (1901).

2 parts of sodium peroxide and finally pouring the brownish yellow fused mass on an iron plate to cool. When cold, wash the mass four or five times by decantation with water, collect on an asbestos filter and dry at 100°. The compound is somewhat unstable and if kept over 6 months it should be tested to see if its oxidizing power is still sufficient. Dark brown samples appear to be just as efficient as those which are yellow.

2. *Nitric Acid.*—For dissolving the sample, use nitric acid (d. 1.13) which may be prepared by diluting concentrated nitric acid (d. 1.42) with three volumes of water. This acid, as it contains 25 per cent of the concentrated acid by volume, will be called the 25 per cent acid (it contains about 22.5 per cent of anhydrous HNO_3 by weight).

For diluting the solution after the bismuthate treatment and for washing the residue on the filter, use 3 per cent nitric acid prepared by mixing 30 c.c. of nitric acid, d. 1.42 with 970 c.c. of water. All the nitric acid used in this analysis must be free from nitrous acid. Since Reynolds and Taylor[1] have shown that nitric acid as weak as 10 per cent is decomposed by light and that recombination takes place in the dark, the bottles of concentrated nitric acid and of 25 per cent acid should be preserved in the dark. Nitrous acid reacts with permanganate precipitating manganese dioxide, so that if nitrous acid is present in the solution treated with bismuthate, some of the manganese may be left on the filter. Moreover, if a ferrous salt is titrated with permanganate in the presence of nitric acid containing some nitrous acid, an excessive amount of permanganate will be required.

3. *Potassium Permanganate Solutions.*—For steels containing less than 1 per cent of manganese 0.03*N* permanganate (0.95 g. $KMnO_4$ per liter) is suitable; for higher manganese content a 0.1*N* permanganate (3.16 g. $KMnO_4$ per liter) should be used. The addition of 10 g. caustic potash per liter lessens the tendency of the permanganate solution to change on standing.[2] The conditions recommended by McBride[3] for standardizing tenth-normal permanganate against sodium oxalate are briefly

[1] *J. Chem. Soc.*, **101**, 131 (1912).
[2] BLUM, *J. Am. Chem. Soc.*, **34**, 1379.
[3] *J. Am. Chem. Soc.*, **34**, 415 (1912).

as follows: Volume, 250 c.c.; acidity, 2 per cent concentrated sulfuric acid by volume; initial temperature, 80 to 90°; slow addition of permanganate especially at the beginning and end; final temperature not less than 60°; end-point correction with a blank containing a known amount of permanganate. For standardizing the 0.03*N* solution not more than 0.075 to 0.1 g. of sodium oxalate should be taken.

4. *Ferrous Sulfate or Ferrous Ammonium Sulfate Solutions.*—There is little choice between these substances as regards the stability of their solutions. For use with 0.03*N* permanganate weight out 12.4 g. of ferrous ammonium sulfate, or 8.8 g. of ferrous sulfate crystals, add 50 c.c. of concentrated sulfuric acid and dilute to 1 liter. For use with 0.1*N* permanganate, take 39.2 g. of ferrous ammonium sulfate or 27.8 of ferrous sulfate and the same volumes of sulfuric acid and water as before. No appreciable change takes place in the ferrous content of these solutions during a period of a few hours. The 0.1*N* ferrous solutions lose about 1 per cent in reducing power in 5 days. The solutions should be titrated against the permanganate, therefore, on the same day that the analyses are made.

To determine the reducing power of the ferrous solutions, take 50 c.c. of 25 per cent nitric acid and add a little sodium bismuthate. Shake and allow to stand a few minutes. Dilute with 50 c.c. of 3 per cent nitric acid, filter through an asbestos filter and wash with 100 c.c. of 3 per cent nitric acid. To the clear filtrate add 50 c.c. of ferrous sulphate, or the amount to be used in the analysis, and titrate at once with permanganate to the first visible pink.

The treatment with bismuthate is not absolutely necessary but it affords a convenient way for testing the efficacy of the filter.

5. *Sodium Arsenite Solution.*—Prepare a stock solution by heating 15 g. of arsenious oxide, As_2O_3, and 45 g. of sodium carbonate with 150 c.c. of distilled water. When the arsenic oxide has all dissolved, dilute the resulting solution of sodium arsenite to a volume of 1 liter. To make the standard solution of sodium arsenite, dilute 300 c.c. of the stock solution with 700 c.c. of distilled water and after standardizing against the permanganate, adjust the solution so that it is 0.0182-normal

when 1 c.c. of solution will be equivalent to 0.100 per cent of manganese on the basis of a 1-g. sample of steel. For the analysis of ordinary steels, three significant figures is all that need be considered in the computation and the sample should be weighed to the nearest centigram.

Procedure for Steels.—Dissolve 1 g. of steel in 50 c.c. of the 25 per cent acid using a 200 to 300-c.c. Erlenmeyer flask. When the steel has all dissolved, boil the solution gently to expel oxides of nitrogen. Cool somewhat and add about 0.5 g. of sodium bismuthate in small portions. It is necessary to add bismuthate until a permanent permanganate color is obtained but a large excess should be avoided.

This preliminary oxidation serves to oxidize the dissolved carbide which might otherwise react with the permanganate after it is formed.

Heat the solution for a few minutes until the pink color of permanganate has disappeared, with or without precipitation of manganese oxide. Add small portions of ferrous sulfate (or any other suitable reducing agent such as sulfurous acid, sodium sulfite, or hydrogen peroxide) to the hot solution in sufficient quantity to dissolve any precipitated manganese dioxide, but carefully avoiding an excess of the reagent. Boil the solution for 2 min. to expel oxides of nitrogen and cool to 15°. To the *cold* solution add a slight excess of sodium bismuthate (usually 0.5 to 1.0 g. is sufficient; an excess makes the subsequent filtration more difficult) and agitate well for at least ½ min. Add 50 c.c. of 3 per cent nitric acid, washing down the sides of the flask, and filter through an alundum crucible or asbestos pad. Wash the residue with 3 per cent nitric acid, using 50 to 100 c.c. and making sure that the last runnings are colorless. A suitable filter may be made by tamping down a wad of glass wool into an ordinary funnel and pouring over it just enough suspended asbestos fibers, such as are used for Gooch crucibles, to form a layer sufficient to hold back the excess of bismuthate. If too much asbestos is used the filter will become clogged too readily.

Titrate immediately with the standard sodium arsenite solution, to the disappearance of the pink color. Or, as many chemists prefer, add enough standard ferrous sulfate solution to decolorize the permanganate (preferably using a 25 or 50-c.c.

pipette) and titrate the excess of the latter with standard permanganate.

Procedure for Cast Iron.—Dissolve 1 g. of metal in 25 c.c. of 25 per cent nitric acid in a small beaker. When all action has ceased, filter into a 200-c.c. Erlenmeyer flask. Wash the filter with 30 c.c. of the 25 per cent nitric acid and proceed as with steels.

The removal of the carbonaceous residue is essential as otherwise it is almost impossible to convert all the manganese to permanganate. If it is desired to test an insoluble residue for manganese, volatilize the silica by treatment with sulfuric and hydrofluoric acids, fuse the residue with a little potassium pyrosulfate (potassium acid sulfate heated until it begins to fume), take up the fusion in 25 per cent nitric acid, and then treat with sodium bismuthate.

In the analysis of white irons, it may be necessary to treat the solution several times with sodium bismuthate in order to destroy all the iron carbide in the preliminary treatment. Otherwise, the carbide will prevent the quantitative conversion of the manganese to permanganate.

Procedure for Ferro-manganese.—Treat 1 g. with 25 per cent nitric acid exactly as in the analysis of steel. Dilute the solution to 500 c.c. in a calibrated flask and take an aliquot part corresponding to from 0.01 to 0.02 g. of manganese. Add 12 to 15 c.c. of concentrated nitric acid (d. 1.42), dilute to 50 or 60 c.c., and treat with sodium bismuthate in the usual way.

Procedure for Ferro-silicon.—Treat 1 g. with sulfuric and hydrofluoric acids and heat until thick fumes of sulfuric acid are evolved. Cool and dissolve in 25 c.c. of 25 per cent nitric acid. Transfer to a 200-c.c. flask, rinse the dish or crucible with 25 c.c. more of the same acid, and proceed as usual.

Procedure for Special Steels.—In modern alloy steels, particularly steels used for self-hardening or high-speed drills, the element chromium is likely to be present and it, like manganese, is easily oxidized by sodium bismuthate. The oxidation of chromium takes place more slowly than that of manganese and, to effect complete oxidation, it is desirable to work at the boiling temperature, in which case the manganese is changed to insoluble manganese dioxide.

During the preliminary oxidation in the above directions, some chromium will always be changed to chromate. If this is carefully reduced with sulfurous acid or sodium sulfite, and the solution is cooled to approximately 0° in ice water, agitation with a slight excess of sodium bismuthate will effect the complete oxidation of the manganese to permanganate and, if there is no delay in filtering or titrating, correct results can be obtained without any appreciable oxidation of chromium.

Many operators, however, find trouble when chromium is present and obtain results for manganese which are too high. To overcome this difficulty, it is advisable to precipitate the chromium as chromic hydroxide by means of zinc oxide suspension[1] (20 g. of ZnO triturated to a paste with a little water and poured into 100 c.c. of distilled water).

Zinc Oxide Modification.—Weigh 2.50 g. of steel into a 300-c.c. casserole, add 45 c.c. of 6-normal sulfuric acid, cover the casserole with a watch-glass and heat until the steel is dissolved. Add 4 c.c. of concentrated nitric acid, to oxidize the iron[2] and evapo-

[1] C. T. Nesbitt (*Chem. News.*, **115**, 64 (1917)) has tested a number of methods for determining manganese in high-speed steels and finds the bismuthate method satisfactory if the tungsten is completely removed, if the chromium is carefully reduced and if the titration with permanganate does not stop until an end-point is permanent for 5 min.

Nesbitt in the analysis of high-speed steels containing chromium recommends the following procedure: Dissolve 1.10 g. of steel in 12 c.c. of concentrated hydrochloric acid. Add 5 c.c. of concentrated nitric acid and evaporate to sirupy consistency. Then add exactly 7 c.c. of concentrated sulfuric acid and wash once round the sides of the beaker with a little water. A thick creamy mass forms on the bottom of the beaker. Leave the beaker near the edge of the hot plate for 20 min. and then fume strongly for 15 min. to make sure that the last traces of chloride are removed. Cool, take up with 30 c.c. of 6-normal nitric acid and 20 c.c. of water. Boil and filter off the tungstic acid with some filter paper pulp on the filter. Wash the filter at least five times and add 15 c.c. of concentrated nitric acid to the filtrate. Add a pinch of sodium bismuthate, boil and carefully decolorize with sulfurous acid. Boil off the excess sulfurous acid, cool to below 15° and continue in the usual way, taking care that there is no delay after the final addition of bismuthate.

[2] If tungstic acid precipitates from the solution at this point it is best to remove it. After the addition of the nitric acid, concentrate to a small volume and dilute with 60 c.c. of 6-normal nitric acid. Filter off the precipitate, using filter pulp to prevent clogging of the paper filter. Then proceed with the neutralization with ZnO in the usual manner.

rate slowly until copious fumes of sulfuric acid are evolved. Cool, add 100 c.c. of water and heat until the sulfates are all dissolved. Cool and transfer the solution to a 500-c.c. calibrated flask. Add sodium carbonate solution (60 g. dissolved in about 100 c.c. of water) until the solution is nearly neutral and the precipitated hydroxides, which form where the sodium carbonate is in excess, redissolve very slowly. Then add small portions of the zinc oxide suspension until, after allowing the precipitate to settle, the supernatant liquid is practically clear. Cool and make up to the mark with distilled water. Mix thoroughly by pouring into a large dry beaker and back again into the flask, repeating the operation several times. Allow the precipitate of ferric and chromic hydroxides to settle and then filter through a dry filter transfer 200 c.c. of the solution (corresponding to 1 g. of steel) by a pipette or graduated flask to a 300-c.c. Erlenmeyer flask, add 25 c.c. of 25 per cent nitric acid and continue as in the usual bismuthate method.

Computation.—One cubic centimeter of normal $KMnO_4$ soln. = 0.03161 g. $KMnO_4$ = 0.06700 g. $Na_2C_2O_4$ = 0.01099 g. Mn. If n c.c. of $KMnO_4$ = p g. of $Na_2C_2O_4$, then the permanganate is $\frac{p}{n \times 0.067}$ normal and 1 c.c. $KMnO_4$ = $\frac{p \times 0.01099}{n \times 0.067}$ g. Mn.

In using the ferrous sulfate method, subtract the number of cubic centimeters of $KMnO_4$ used in the analysis from the cubic centimeters of $KMnO_4$ equivalent to all the ferrous solution used and the difference gives the volume of $KMnO_4$ solution which is equivalent to the manganese in the sample.

With the sodium arsenite solution, if r c.c. $KMnO_4$ = r_1 c.c. of sodium arsenite, then 1 c.c. Na_2HAsO_3 solution = $\frac{r \times p \times 0.01099}{r_1 \times n \times 0.067}$ g. Mn. If s represents the weight of sample, n_1 the number of cubic centimeter of permanganate used in titrating the excess of ferrous solution, n_2 the number of cubic centimeters of permanganate equivalent to the entire quantity of ferrous salt added, and T the value of 1 c.c. permanganate in terms of Mn, then

$$\frac{(n_2 - n_1)\, T \times 100}{s} = \text{per cent Mn}$$

Accuracy of the Method.—When the conditions are right, the bismuthate process is certainly as accurate as any known method for determining manganese in solutions containing less than 0.05 g. of the element. In the analysis of samples rich in manganese, satisfactory results are obtained by using an aliquot part of the original solution. Blum[1] tested the method in four ways: with a manganese sulfate solution of known manganese content, by reducing a measured volume of permanganate and oxidizing it again with sodium bismuthate, by analyzing potassium permanganate crystals and by analyzing a standard manganese ore. Concordant results within 1 part in 500 were obtained. The oxidation of the manganese to permanganate is quantitative in well-agitated solutions at temperatures below 25° and the acidity of the solution, when the bismuthate is added, may vary between 20 and 40 per cent in a volume of 50 to 150 c.c. The preliminary treatment with sodium bismuthate should never be omitted and any difficultly soluble residue containing oxidizable material must be removed by filtration, as mentioned in the above directions. The electrometric titration of manganese will be described in Chap. XX.

2. DETERMINATION OF MANGANESE BY THE FORD-WILLIAMS METHOD

This method depends upon the precipitation of manganese dioxide by the addition of potassium chlorate in nitric acid solution and is the best known of those methods which separate iron and manganese by the precipitation of the latter. In England and in the United States the process is usually attributed to Williams[2] or to Ford[3] and Williams but in Germany it is credited to Hampe[4] or to Beilstein and Jawein. When potassium chlorate is added to a solution containing manganese ions in the presence of strong nitric acid, the following reaction takes place:

$$Mn^{++} + 2ClO_3^- = MnO_2 + 2ClO_2$$

The manganese dioxide is obtained as a precipitate and the

[1] *Loc. cit.*

[2] *Trans. Inst. Mining Engineers*, **10**, 100.

[3] *Ibid.*, **9**, 397.

[4] *Chem. Ztg.*, **7**, 73.

chlorine dioxide is boiled off as a gas. The precipitate may be dissolved in a measured volume of acid ferrous sulfate solution or hot oxalic acid solution:

$$MnO_2 + 2Fe^{++} + 4H^+ = Mn^{++} + 2Fe^{+++} + 2H_2O$$
$$MnO_2 + 4H^+ + C_2O_4^{--} = Mn^{++} + 2CO_2 + 2H_2O$$

and the excess of reducing agent determined by titration with permanganate.

This method, like the bismuthate method already described, is recommended by the American Society for Testing Materials for the determination of manganese in cast iron. It is capable of giving excellent results in the analysis of steels although not as sensitive as the bismuthate method for determining small quantities of manganese and not as reliable as the Volhard method for determining large quantities of manganese.

Solutions Required.—*Nitric Acid.*—For dissolving the sample use nitric acid, d. 1.42 diluted with an equal volume of water. This acid is approximately 8-normal. The undiluted acid is always understood when the words *concentrated nitric acid* are used.

Standard Ferrous Sulfate Solution.—Dissolve 10 g. of pure $FeSO.7H_2O$ in 900 c.c. of water and 100 c.c. of concentrated sulfuric acid. The presence of the sulfuric acid prevents the precipitation of insoluble basic ferric salt which will otherwise form when the solution is oxidized by dissolved oxygen. The solution oxidizes slowly on standing and must be standardized when used.

Standard Permanganate, about 0.03-normal. Dissolve about 1 g. of permanganate in each liter of water. Allow the solution to age by standing some days or by boiling it.[1] Filter through glass wool tamped down in a funnel and covered with a thin layer of asbestos. Use the first runnings to rinse out the care-

[1] If the permanganate is perfectly pure and is dissolved in water that has been doubly distilled, the last time with permanganate in the still, the solution will keep indefinitely if protected from light and dust. Ordinary distilled water contains a small quanty of volatile protein which reacts with permanganate. Reducing gases when dissolved in water have the same effect. When properly aged and then filtered the permanganate solution is very stable. When it once begins to decompose the precipitated MnO_2 acts as a catalyzer so that the rate of decomposition increases.

fully cleansed stock bottle. To standardize the solution, weigh out 0.2 to 0.3 g. of pure sodium oxalate, dissolve in 250 c.c. of water containing 2 c.c. of concentrated sulfuric acid and heat to about 90°. Titrate very slowly with permanganate, particularly at the beginning and end, and take care that the final temperature is not less than 50°. The values of 1 c.c. $KMnO_4$ in terms of sodium oxalate should agree within 0.2 per cent. Since the equivalent weight of sodium oxalate is 67 (one-half the molecular weight) the normal concentration of the permanganate is found by dividing the value of 1 c.c. in terms of sodium oxalate by 0.067.

Procedure.—Dissolve 3 g. of the sample (weighed to the nearest centigram) in 40 c.c. of 8-normal nitric acid. In the analysis of irons filter off the insoluble residue of silica and carbon. Concentrate the solution to sirupy consistency in a 600-c.c. Erlenmeyer flask, add 40 c.c. of concentrated nitric acid and 3 g. of potassium chlorate and boil the solution for 15 min. Remove from the source of heat, as otherwise ClO_2 may explode, add 15 c.c. more of concentrated nitric acid, another 3-g. portion of potassium chlorate and boil again until yellow fumes cease to come off. Cool quickly, by placing the flask in cold water and rotating the contents, and filter the precipitated manganese dioxide on asbestos. A satisfactory filter is obtained by placing a little glass wool in an ordinary funnel and pouring on it a little suspended asbestos fibers, such as are used for Gooch crucibles. Wash the precipitate with concentrated nitric acid till free from iron and with water till free from acid. Transfer the asbestos pad and precipitate to the original flask, cover with 50 c.c. of standard ferrous sulfate solution and dilute with water to a volume of 200 c.c. Shake the contents of the flask with small pieces of glass stirring-rod to break up the precipitate, until the manganese is all dissolved, and then titrate with 0.03-normal permanganate. The ferrous sulfate solution must be standardized against the permanganate solution the same day the analysis is made. Measure out 50 c.c. of the solution, dilute to 200 c.c. and titrate with permanganate.

Computation.—If a c.c. of $KMnO_4$ solution react with p g. of pure $Na_2C_2O_4$, if 50 c.c. of $FeSO_4$ solution react with b c.c. of $KMnO_4$ and if c c.c. of $KMnO_4$ are used in the analysis of the

solution from 3 g. of metal which has been treated with 50 c.c. of $FeSO_4$ soln. Then

$$\frac{p \times 1.099}{a \times 0.067 \times 3}\left(b - c\right) = \text{per cent Mn}$$

Accuracy of the Method.—The precipitate formed by treatment with potassium chlorate is assumed to contain all the manganese in the quadrivalent condition. This is probably not strictly true. Moreover, if the conditions are not right, often some of the manganese is not precipitated. If the manganese dioxide precipitate stands for some time it becomes less readily soluble in the ferrous sulfate solution. In spite of these objections, however, the results obtained are usually satisfactory and the method is more suitable than the Volhard method for steels containing less than 0.6 per cent manganese.

3. DETERMINATION OF MANGANESE BY THE VOLHARD METHOD

This method has always been a favorite one in Germany and there are over 50 publications concerning it in scientific journals since 1879.

(A) Modified Volhard Method

Principle.—Manganous salts react with permanganate in accordance with the following equation:

$$2MnO_4^- + 3Mn^{++} + 2H_2O = 5MnO_2 + 4H^+$$

Gorgeu[1] first attempted to use this reaction as a basis for the volumetric determination of manganese but Volhard is generally considered to be the father of the method in its present form.[2]

The conditions necessary to carry out the reaction strictly in accordance to the above equation, in the analysis of a solution of manganous salt containing a large quantity of ferric chloride, are obtained most readily by precipitating the iron from a hot, dilute solution with a slight excess of zinc oxide, adding quickly an excess of potassium permanganate, and titrating the excess of the latter in a suitable manner.

[1] *Ann. chim. phys.*, III, **66**, 154 (1862).

[2] Deiss, *Chem. Ztg.*, **34**, 237 (1910).

If the conditions are not quite right it is possible that the reaction between the manganous salt and the permanganate may take place differently. Thus, for example, in Wolff's[1] method where the permanganate is added gradually after the iron has been precipitated by the zinc oxide, less permanganate is required to precipitate all the manganous salt, and, within certain limits, the volume of permanganate required is smaller in proportion as the amount of zinc oxide added is large. In some cases the error may amount to 10 per cent of the total manganese content.

If the zinc oxide excess is equal to zero, so that only ferric hydroxide is present (a condition difficult to fulfil) then the permanganate consumption by the Wolff method corresponds to that required by the equation.

The reason for low results when an excess of zinc oxide is used is chiefly due to the fact that some of the manganese is precipitated with the ferric hydroxide.

When the titration of the manganous salt by permanganate is carried out in a slightly *acid* solution, as recommended by Volhard, the results are lower than the equation demands. In this case the error is due chiefly to the fact that the manganese dioxide precipitate, as it forms slowly, carries with it some adsorbed manganous oxide and thereby escapes reaction with the permanganate.

In the modification suggested by Schöffel and Donnath, the manganous chloride solution containing suspended ferric hydroxide, formed by the addition of an excess of zinc oxide, is added to an excess of permanganate solution; correct results may be obtained if the two solutions are mixed quickly enough. The condition of having permanganate always present in excess is not alone sufficient to prevent disturbances such as are likely to result in the method of Volhard and Wolff.

In using the Wolff method it is often proposed to avoid error by using an empirical factor for the permanganate solution instead of the theoretical value as established by equations. Since, however, the factor varies with the amount of zinc oxide added to precipitate the iron, it is evident that this method is not altogether satisfactory.

[1] *Stahl u. Eisen*, **1884**, 702; **1891**, 377.

Probably the most successful expedient, and one that gives good results in the hands of a skilful worker, is to standardize the permanganate solution against a manganous solution of known content in exactly the same way in which the analysis is to be carried out.

Requisite Apparatus and Solutions.—In carrying out the titrations, it is convenient to have at hand a wooden frame, Fig. 12, fitted to hold in an inclined position two flasks of 1.1 to 1.5 liters capacity. The hollows in which the bottoms of the flasks rest are covered with felt to prevent breakage. In carrying out a titration, the frame is placed upon the working bench so that the middle of the flask is at about on a level with the eye, in such a way that there is a background of a window on which the sun is not shining.

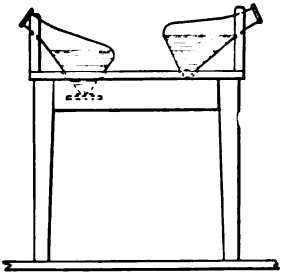

FIG. 12.

For the titration, the following solutions are used:

1. *Potassium Permanganate Solutions.*—It is well to have two solutions of permanganate on hand, a weaker solution containing about 16 g. of potassium permanganate in 5 liters of water and a stronger one containing about 40 g. of the permanganate in the same volume of solution.

The solutions are prepared by dissolving weighed portions of pure potassium permanganate in a beaker using distilled water that has been recently boiled and allowed to cool.[1] The solution is decanted off from time to time into a clean 5-liter flask and eventually diluted up to the mark. Before using them for titrations, the permanganate solutions should stand in stoppered bottles for from 8 to 14 days, protected from light and dust. At the end of this time any oxidizable matter in the solution will have reacted with the permanganate and any manganese dioxide present as colloid in the freshly prepared solutions will have deposited on the bottom or sides of the bottle in the form of a brown precipitate. The solutions should then be

[1] The addition of 10 g. caustic potash per liter retards the decomposition of permanganate by dust, reducing gases, or precipitated manganese dioxide. BLUM, W., *J. Am. Chem. Soc.*, **34**, 1379.

filtered through asbestos. If protected from light and dust (filtering the air entering the bottle through alkaline permanganate) the filtered solution will keep indefinitely.[1]

2. *Sodium Arsenite Solutions.*—The strength of two arsenite solutions are chosen preferably so that 1 c.c. of permanganate is equivalent to about 2 c.c. of arsenite. To prepare the weak and strong solutions, weigh portions of 8 and 20 g. of pure arsenic trioxide into beakers containing half as much pure sodium hydroxide. Dissolve in a little water, with heating, filter if necessary, and dilute each solution to a volume of 5 liters.

Standardization of the Permanganate Solutions

(*a*) *Against Sodium Oxalate.*—Standardize as described on page 50 using about 0.3 g. of oxalate for the weaker solution and 0.8 g. for the stronger solution. The reaction that takes place in the titration may be expressed as follows:

$$2MnO_4^- + 5C_2O_4^{--} + 16H^+ = 2Mn^{++} + 10CO_2 + 8H_2O$$

Thus, 2 molecules of permanganate will oxidize 5 molecules of oxalate and we have seen that 2 molecules of permanganate oxidize 3 molecules of manganous salt to manganese dioxide. Five molecules of sodium oxalate (670.0 g.) are equivalent, therefore, to 3 molecules of manganous salt (164.79 g. of manganese.)

If a g. of sodium oxalate require n c.c. of permanganate, then

$$1 \text{ c.c. } KMnO_4 \text{ soln.} = \frac{164.8 \times a}{670.0 \times n} = 0.2460 \frac{a}{n} \text{ g. Mn}$$

This factor applies only to the Volhard method.[2]

(*b*) *Against Sodium Thiosulfate Solution.*—When potassium permanganate is added to an acid solution of potassium iodide, the following reaction takes place:

$$2MnO_4^- + 10I^- + 16H^+ = 2Mn^{++} + 8H_2O + 5I_2$$

and the free iodine may be titrated with sodium thiosulfate.

$$I_2 + 2S_2O_3^{--} = 2I^- + S_4O_6^{--}$$

[1] *cf.* Morse, Hopkins and Walker, *Am. Chem. J.*, **18**, 401; Gardner and North, *J. Soc. Chem. Ind.*, **23**, 599; Warynski and Tscheischwili, *J. chim. phys.*, **6**, 567; Treadwell-Hall, "Quantitative Analysis," II, 603 (1914).

[2] *Ann.*, **198**, 333, **242**, 98 (Volhard).

If the strength of either the permanganate or of the thiosulfate solution is known, that of the other solution may be computed.[1] The reaction furnishes a rapid and accurate method of standardization.

Dissolve about 2 g. of pure potassium iodide in 300 c.c. of water, add 5 c.c. of dilute hydrochloric acid (d. 1.12) and if the solution is at all yellow (free iodine liberated by iodate in the iodide or of free chlorine in the acid) carefully discharge the color by the addition of a drop or more of dilute thiosulfate solution. Add to the colorless solution of potassium iodide an accurately measured volume of the permanganate solution, using 50 c.c. in the case of the weaker solution and 25 to 30 c.c. of the stronger. The solution is at once colored red by the liberated iodine.[2] In case a precipitate of manganese dioxide is formed, dissolve it by the addition of a little more hydrochloric acid. Titrate the solution with tenth-normal sodium thiosulfate until nearly colorless, than add a little starch solution[3] and finish the titration.

Computation.—The above equations show that 2 molecules of permanganate liberate 10 atoms of iodine which in turn react with 10 molecules of thiosulfate. In the titration of the manganous salt by permanganate, we have seen that 2 molecules of permanganate react with 3 molecules of manganous salt. Thus, 3 atoms of manganese in the bivalent condition have the same reducing power as 10 molecules of thiosulfate and 1 c.c. of tenth-normal thiosulfate is equivalent to $\frac{3 \times \text{Mn}}{10 \times 1000} = 0.3 \times 0.05493 =$ 0.001648 g. Mn. If, in the standardization, n c.c. of tenth-normal thiosulfate are equivalent to a c.c. of permanganate.

$$1 \text{ c.c. } KMnO_4 \text{ solution} = 0.001648 \frac{n}{a} \text{ g. Mn}$$

[1] It is possible to prepare perfectly pure, anhydrous thiosulfate (*cf.* YOUNG, *J. Am. Chem. Soc.*, **26**, 1028) and with this salt it is easy to prepare a tenth-normal solution.

[2] The iodine really unites with unchanged iodide ions to form I_3^- ions in which two-thirds of the iodine behaves like free iodine.

[3] Zinc-iodide-starch solution can be bought which is suitable for such titrations or a starch solution may be prepared by dissolving 0.5 g. of soluble starch in 25 c.c. of hot water.

The results obtained by this method of standardization agree closely with those obtained by standardizing against sodium oxalate. There is little choice between the two methods. The standardization of the arsenite solutions is explained in the description of the method of analysis.

Method of Carrying Out the Analysis

(*a*) *Preparation of the Sample for the Titration.*—If the manganese alone is to be determined in an alloy containing less than 10 per cent of this element, proceed in the following manner:

Weigh out three separate portions,[1] each containing 2 g. of material, into a porcelain dish of 12 cm. diameter. Cover the dish with a watch-glass and dissolve each sample by the gradual addition of 25 c.c. of nitric acid (d. 1.2). When solution is complete, remove the watch-glass, evaporate to dryness, and destroy the nitrates by igniting at first over asbestos and finally over the free flame until no more nitrous fumes are evolved. Cool and take up the residue in about 20 c.c. of concentrated hydrochloric acid (d. 1.2).

If a dark-colored residue (containing graphite) remains undissolved, evaporate the hydrochloric acid solution to dryness, dehydrate any silicic acid by heating to 125°, redissolve in hydrochloric acid, dilute, filter and wash the residue thoroughly before proceeding with the titration. The undivided solution is used.

If graphite is not present, it is unnecessary to filter off the silica. Evaporate the hydrochloric acid solution of the oxides to dryness, to remove any chlorine that may have been formed from the interaction of manganomanganic oxide and hydrochloric acid. take up the residue in hydrochloric acid (d. 1.12) and rinse the solution into an Erlenmeyer flask of about 1 liter capacity. The solution is now ready for titration.

If it is desired to combine the manganese determination with the determination of silicon, or phosphorus in samples rich in phosphorus, or nickel in a nickel steel, a larger quantity of material may be taken for the analysis and an aliquot part of

[1] One sample is to be used for a preliminary titration which does not, as a rule, give exact results.

the solution used for the manganese determination. In this way a better average sample is obtained. Of materials containing up to 10 per cent manganese, from 8 to 10 g. are taken, of richer manganese alloys (ferro-manganese, metallic manganese, etc.) a correspondingly smaller amount (down to 2 g.). Dissolve the sample in nitric acid (d. 1.2) and remove the silica as described on p. 64.

Catch the filtrate from the silica in a 500-c.c. calibrated flask, or, if the weight taken was less than 8 or 10 g., in a 250-c.c. flask. If a dark-colored residue remains after volatilization of the silicon by treatment with sulfuric and hydrofluoric acids, dissolve it in the crucible with a little hydrochloric acid (d. 1.12) and rinse the solution into the calibrated flask.

Fill the flask up to the mark with water which is at the laboratory temperature, thoroughly mix by pouring back and forth into a dry beaker several times, and take an aliquot part for the manganese determination by means of a pipette, a smaller calibrated flask, or by weighing.

If the substance for analysis is insoluble in acids, ignite from 2 to 3 g. with magnesia and sodium carbonate as described for the determination of silicon, p. 124. Transfer the ignited mass from the crucible to an agate mortar, moisten with water, break up the larger pieces with the pestle and grind into a fine powder. Rinse the mass into a beaker, cover the latter with a watch-glass and add a little sodium peroxide to decompose any manganate that was formed during the ignition. Heat the liquid on the water bath, with frequent stirring, until the excess of peroxide is decomposed and, if the solution then appears green or violet (from manganate or permanganate), repeat the treatment with sodium peroxide. After the manganate has all been reduced, the solution should be colorless, or yellow in case chromium is present. Filter off the precipitate, containing all the manganese and iron together with the magnesia, etc., and wash it well with hot water. Rinse the precipitate into a porcelain dish and dissolve it in hydrochloric acid (d. 1.12). Evaporate the solution nearly to dryness, to make sure that all the chlorine is expelled, and rinse with dilute hydrochloric acid into a 250-c.c. calibrated flask. Make up to the mark with water and take an aliquot part for the titration.

The quantity of manganese to be titrated determines which of the two permanganate solutions should be used. In general, solutions containing from 40 to 80 mg. of manganese (corresponding to a 2-g. sample with 2 to 4 per cent manganese) may be titrated with the weaker solution; if the manganese content is higher the stronger solution should be used.

If the sample contained only a little iron, add enough pure ferric chloride to each solution before titration so that the iron content will correspond to about 1 g. of metal. For this purpose, it is well to have at hand a solution of ferric chloride made by dissolving about 500 g. of pure ferric chloride ($FeCl_3 + 6H_2O$) in water with a little hydrochloric acid and diluting to 1 liter; such a solution contains about 1 g. of iron in 10 c.c.

(*b*) *Titration of the Solution.*—The solution to be titrated, prepared as just described, should be in an Erlenmeyer flask of about 1 liter capacity. To oxidize traces of ferrous salt that may be present, add a small crystal of potassium chlorate or, better, a few drops of pure, concentrated hydrogen peroxide solution[1] and boil gently for 10 or 15 min. to destroy the excess of oxidizing agent (replacing the hydrochloric acid lost by evaporation). There should be no odor of free chlorine.

Meanwhile heat the distilled water necessary for the titration to boiling in a 2-liter flask and triturate the zinc oxide necessary for the precipitation of the iron in a mortar with water, until a thin paste is obtained. This may be kept in a small Erlenmeyer flask. If the approximate manganese content of the solution is not known, determine it by a trial titration carried out in the following manner:

Dilute the manganese solution in the Erlenmeyer flask with boiling water until the volume is about 600 to 700 c.c. Add the suspension of zinc oxide in small amounts until, after vigorous shaking, all the iron is precipitated in the form of brown ferric hydroxide[2] and the solution is clear and colorless after the precipitate settles.

[1] Perhydrol.

[2] It is not necessary to add zinc oxide until the excess whitens the precipitate. There is no danger of an excess of zinc oxide doing any harm, however, provided the permanganate solution is added rapidly, as in the main analysis.

For convenience, place the flask in an inclined position in the support described on p. 61 while the precipitate is settling. Add 10 c.c. of the permanganate solution from a burette, shake vigorously and replace the flask upon the support. If, when the precipitate settles, the supernatant liquid is uncolored by permanganate, add another 10 c.c. of permanganate, shake and again allow to settle. Repeat the operation until the solution above the precipitate is colored by permanganate. Then add the corresponding arsenite solution in small quantities, shaking and allowing to settle after each addition. Continue to add arsenite solution until the permanganate is decolorized.

From the volumes of permanganate and arsenite solutions used in this trial titration, the approximate volume of permanganate required can be computed by assuming the two solutions to be of the same strength. The exact value of the arsenite solution is determined at the time the accurate titration is made.

For this accurate titration of the manganese content of the solution, measure from a burette, into a small beaker, from 2 to 4 c.c. of permanganate more than that found necessary by the trial titration. Then dilute the manganese solution containing ferric iron to a volume of 600 to 700 c.c., add the necessary quantity of zinc oxide suspension, and shake well. When all the iron is precipitated, quickly add the permanganate solution from the beaker, rinse the beaker, and shake the contents of the flask vigorously.

If the solution should now be colorless, or show only a very pale permanganate color, it is best to repeat the experiment using a somewhat larger quantity of permanganate.

To determine the excess of permanganate, add the arsenite solution in small portions from a burette, shaking and allowing to settle each time, until the supernatant solution is colorless. It is necessary, toward the last, to add but a drop or two of arsenite solution at a time.

To determine the reducing action of the arsenite under as nearly as possible the same conditions, add 5 c.c. of permanganate from a burette to the hot solution that has just been titrated, and again titrate with arsenite solution until the permanganate is all decolorized. In this way the value of 1 c.c. of arsenite solution in a cubic centimeter of permanganate is determined, and the

exact volume of permanganate required to react with the manganese in the analyzed sample can be computed.

If ferric chloride solution was added, then an equally large volume of it should be diluted with hot water, treated with zinc oxide suspension and titrated with permanganate until a pink color is obtained. The volume of permanganate used here should be deducted from that used in the main experiment.

Computation.—Let s represent the weight of sample, a_1, the number of cubic centimeters of permanganate used in the main titration, b_1, the number of cubic centimeters of arsenite solution used in the main titration, a_2 the number of cubic centimeters of permanganate added afterward, b_2 the number of cubic centimeters of arsenite required to react with this last permanganate, c the number of cubic centimeters of permanganate required by the ferric chloride solution if any were used, and T the value of 1 c.c. of permanganate solution in terms of metallic manganese. Then:

$$\frac{[a_1 - b_1 \cdot \frac{a_2}{b_2} - c] \times T \times 100}{s} = \text{per cent Mn}$$

Test Analyses.—The method has been tested by taking an accurately measured volume of permanganate solution,[1] reducing it by evaporation with hydrochloric acid, and then titrating with the addition of ferric chloride solution in exactly the same way as in any analysis. The results show that the reaction takes place strictly in accordance with the equation given when the above-described method is used.

Purity of the Zinc Oxide.—Each new lot of zinc oxide should be tested to see if it is sufficiently pure. Dilute 10 c.c. of ferric chloride solution with hot water to a volume of about 600 c.c., add 4 g. of zinc oxide which has been rubbed into a paste with water, and titrate with permanganate. Repeat the experiment with 10 c.c. of ferric chloride solution, 15 c.c. of hydrochloric acid (d. 1.12) and 10 g. of zinc oxide. If the zinc oxide is pure the permanganate consumption will not be greater in the second case than in the first.

[1] *cf.* WOLFF, *Stahl u. Eisen*, **11**, 380; DE KONINCK, *Bull. soc. chim. Belgique*, **18**, 56.

Accuracy of Results Obtained by the Modified Volhard Method

The manganese content of a solution containing manganous salt and ferric chloride may be determined within a fraction of a milligram. Too high values are often obtained when the solutions contain substances other than manganous salt which can react with permanganate.

Such substances are chromium, cobalt and vanadium. In the analysis of most kinds of ordinary steel these elements are present only to an inappreciable extent.

Repeated determinations of chromium in ordinary grades of iron and steel to which no chromium was intentionally added, have shown that chromium in small amounts is likely to be present and as a result the Volhard method is likely to give too high values. This, together with the difficulty in obtaining the correct end-point make the method less suitable for the determination of quantities of manganese less than 1 per cent than either of the other volumetric methods to be described.

Usually it is possible to obtain duplicate determinations that agree within the following limits:

Manganese content	Permissible deviation
1 to 2 per cent	0.04 per cent
2 to 10 per cent	0.06 per cent
10 upwards	0.1 per cent

It is difficult to get good results by this method in the analysis of nickel steels. This is partly because the yellowish green color of nickel solution and the violet of permanganate are complimentary colors and at the right concentration give a colorless solution. The chief trouble, however, is due to the small quantity of cobalt which is usually present. Cobaltous salts are oxidized by permanganate with the formation of insoluble cobaltic oxide.

4. DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD[1]

In a boiling solution of a manganous salt, ammonium persulfate converts all the manganese to permanganate if a small

[1] *cf.* Walters, *Proc. Eng. Soc. Western Penna.*, **17**, 257 (1901); *Chem. News*, **84**, 239.

amount of dissolved silver salt is present as catalyzer. In the absence of the catalyzer all the manganese is precipitated as dioxide. A number of methods have been worked out on the basis of each of these reactions.

The American Society for Testing Materials recommends the method to be described, which depends upon the formation of permanganate, for routine work in the analysis of steel. The method is not as reliable as the bismuthate method. There is some difficulty in getting ammonium persulfate of suitable purity and permanganate is not very stable in a hot solution but the excess of reagent is decomposed by boiling the solution and does not have to be filtered off as in the bismuthate process. This results in a saving of time.

The reaction of oxidation may be expressed as follows:

$$2Mn^{++} + 5S_2O_8^{--} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{--} + 16H^+$$
$$2H_2O + 2S_2O_8^{--} \rightarrow 4SO_4^{--} + 4H^+ + O_2 \uparrow$$

The reaction of titration is the same as in the bismuthate method.

Procedure.—Dissolve 0.1 to 0.3 g. of steel in 15 c.c. of 25 per cent nitric acid (see Bismuthate method) in a small Erlenmeyer flask or large test tube. Boil gently until the solution is complete and the liquid is clear. Add 15 c.c. of 0.08-normal silver nitrate solution (1.33 g. of silver nitrate per liter) and 1 g. of ammonium persulfate and continue heating for ½ min. after the oxidation begins and bubbles of oxygen rise freely. Cool, by placing the flask under running water, and complete the determination by either of the following procedures:

(*a*) *Colorimetric.*—Compare the color of the solution with that of a standard steel similarly treated.

(*b*) *Titration.*—Titrate with standard sodium arsenite solution to the disappearance of the pink color. (See Bismuthate method.)

5. GRAVIMETRIC DETERMINATION OF MANGANESE

This method is given last because it involves more manipulation than any of the preceding methods and, for this reason alone, is not suitable for a busy laboratory although it may well serve as a reliable method for use in judging the accuracy of other methods.

Principle.—One of the best methods for separating manganese from iron in the analysis of cast iron, steel and other alloys low in manganese, is the Rothe ether separation which is based upon the fact that ferric chloride is very soluble in ether whereas manganese chloride is not.

If two non-miscible solvents are in contact with one another and a third substance is present which is soluble in both liquids, the ratio of the concentrations (quantities present in a unit of volume of each solvent) of this substance in the two solvents after equilibrium has been established will be constant at any given temperature provided the solute has the same molecular weight in both solutions. This is the so-called *distribution law.* The ratio $\frac{c_1}{c_2} = k$, where c_1 represents the concentration in one solution and c_2 the concentration in the other, is called the *distribution coefficient.*

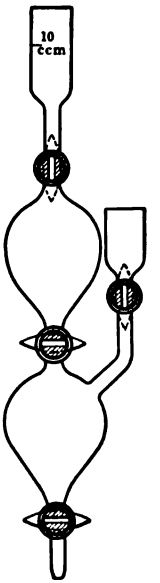

FIG. 13.

After removing the ferric chloride by shaking the hydrochloric acid solution with ether, it is then a question of separating the manganese from other metals and acids that are not dissolved by the ether but remain in the aqueous acid solution.

Requisite Apparatus and Solutions.—For separating ferric chloride from the chlorides of manganese, nickel, aluminium, etc., the Rothe shaking funnel shown in Fig. 13 is suitable.[1] To accomplish a satisfactory separation of the iron from the manganese it is desirable to have on hand 1 or 2 liters of the following solutions:

1. *Hydrochloric Acid* (*d.* 1.10).

2. *Ether-hydrochloric Acid, A.*—Hydrochloric acid (d. 1.19) saturated with ether. To prepare this reagent, ether is added gradually, in small portions, to hydrochloric acid (d. 1.19),

[1] The apparatus can be purchased in two sizes; with each funnel holding about 110 c.c., suitable for the analysis of 5 g. of steel or less, and with each funnel holding about 250 c.c., suitable for the analysis of 15 g. of steel.

until a layer of ether is formed on top of the acid. Considerable heat is evolved as the ether dissolves in the acid, so that it is advisable to cool the solution from time to time by allowing cold water to run over the bottle while it is being shaken. One hundred cubic centimeters of hydrochloric acid (d. 1.19) will dissolve about 150 c.c. of ether.

3. *Ether-hydrochloric Acid, B.*—This is prepared in the same way with ether and hydrochloric acid (d. 1.10). One hundred cubic centimeters of hydrochloric acid (d. 1.10) will dissolve about 30 c.c. of ether.

In separating the manganese from the other metals that are left in the hydrochloric acid solution, a spacious platinum dish, 11 to 13 cm. in diameter, is required and should have handles soldered to opposite parts of the upper edges. For holding the dish, Rothe recommends using small clamps as shown in Fig. 14.

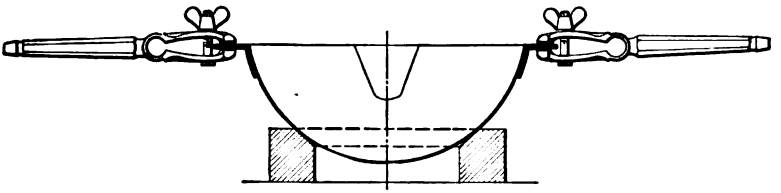

FIG. 14.

Procedure.—Weigh out 10 g. of material containing up to 1 per cent manganese, or 5 g. if the manganese content is higher, into a porcelain dish of 14 or 15 cm. diameter, cover the dish with a watch-glass, and dissolve the sample by the gradual addition of dilute nitric acid (d. 1.18). Continue the treatment exactly as described for the determination of Silicon by Method 1*B*.[1]

[1] Instead of using the filtrate from the silicon determination by Method 1*B*, that from Method 1*A* may be taken. In this case it is necessary to make sure that all the iron is converted into ferric chloride. To this end, concentrate the filtrate from the silicon determination in a porcelain dish until a crust (ferrous chloride) begins to form on the edges of the solution. Then cover the dish with a watch-glass and add dilute nitric acid (d. 1.18) to the hot hydrochloric acid solution as long as the latter is colored dark brown and nitric oxide is evolved. When the oxidation of the iron is complete, wash off the cover glass and evaporate with hydrochloric acid (d. 1.10) to expel the excess nitric acid. The concentrated solution is then ready for the ether separation.

If, after volatilizing the silica by treatment with sulfuric and hydrofluoric acids, a dark-colored residue is obtained, this must be treated by itself for manganese, fusing with sodium hydroxide and sodium peroxide as described on p. 76.

Evaporate the filtrate from the silicon determination in a procelain dish until it becomes very viscous but without the separation of any crystals. The solution is then ready for the ether separation. Pour the concentrated ferric chloride solution into the upper bulb of the shaking funnel (Fig. 13) and rinse out the dish several times with a little hydrochloric acid (d. 1.10) using only 1 or 2 c.c. of the acid for each rinsing; when the last portion of acid added to the dish is not colored yellow by ferric chloride, the washing is complete. It is important at this point to avoid the use of too much hydrochloric acid because the ether separation is most successful when the volume of the hydrochloric acid solution is kept as small as possible. With a little care it is possible to wash out the dish thoroughly without using more than 10 or 15 c.c. of the acid. When all the ferric chloride solution has been transferred to the upper bulb of the shaking funnel, shake the solution, and, as considerable heat is evolved, cool to below 15° by holding the bulb under a stream of running water. If the solution is warm when the ether is introduced, some of the ferric chloride is reduced by the ether and the resulting ferrous chloride is left with the manganese chloride in the hydrochloric acid solution.

According to Rothe's directions for removing ferric chloride by ether from a solution in aqueous hydrochloric acid, it is next necessary to add ether-hydrochloric acid solution *A* until 6 c.c. of the latter are present for each gram of dissolved iron. Shake the solution and cool. This addition of the ether-hydrochloric acid serves partly to give the proper hydrochloric acid concentration for a successful separation by ether and it also serves to prevent, as far as possible, the evolution of heat which takes place when ether is added to a hydrochloric acid solution of ferric chloride.

Next, add ether until the upper bulb is nearly full, close the stopcock and shake. If the upper bulb becomes at all warm, cool under running water.

Fasten the shaking funnel, at the narrow part above the upper

bulb, in a clamp attached to a ring stand and allow the liquid to remain quiet for some time. In this way, two layers are obtained. The upper layer is green and consists chiefly of ferric chloride dissolved in ether. The lower layer consists of a hydrochloric acid solution containing the chlorides of most of the other constituents of the material which is being analyzed. Some hydrochloric acid is present in the ether solution and some ether is present in the lower layer. The color of the latter depends upon what metals other than iron are present in the original substance.

When chromium, nickel or much vanadium is present, the color of the aqueous hydrochloric acid solution is green or bluish-green; if these elements are absent the solution is usually yellow owing to the presence of small quantities of ferric chloride. Often, a brownish-yellow solution is obtained when titanium is present; with considerable titanium and insufficient acid it sometimes happens that flakes of titanium dioxide are deposited (see Titanium).

By opening both the upper and middle stopcocks, allow the hydrochloric acid solution to run into the lower bulb but take care to close the middle stopcock as soon as the line of demarcation between the two layers of liquid is reached; none of the upper ethereal solution should pass into the middle lower bulb at this time, or into the boring of the middle stopcock. Allow the solution in the upper bulb to stand a little longer and again drain off the hydrochloric acid. To wash out the boring of the middle stopcock, add a few cubic centimeters of ether-hydrochloric acid solution *B*, and, without shaking, drain off into the lower bulb the acid that collects below the ether. The upper bulb now contains an olive green solution chiefly of ferric chloride and hydrochloric acid in ether, and the lower bulb contains an aqueous hydrochloric acid solution of the chlorides of manganese, nickel, cobalt, etc. To remove small quantities of these last elements that remain adhering to the ether solution in the upper bulb, add 10 c.c. of ether-hydrochloric acid solution *B*, and to remove small quantities of ferric chloride that are present in the solution contained in the lower bulb, nearly fill it with ether. Close both stopcocks and shake well. After the layers have formed again, the lower layer in the upper bulb contains some more of the manganese, etc., together with a little ferric chloride that has been shaken out of the ether. In the lower bulb, how-

ever, the bottom layer ought not to contain more than 1 or 2 mg. of iron. It is the purpose of subsequent treatment to remove all the metal chlorides except ferric chloride from the ether layer in the upper bulb and to free these hydrochloric acid extracts from iron as far as possible by shaking in the lower bulb with ether containing very little ferric chloride.

Allow the hydrochloric acid solution in the lower bulb to run into the porcelain dish that was used previously in the analysis, and rinse out the boring of the stopcock and the tubing below it with a few cubic centimeters of ether-hydrochloric acid solution *B*. Then allow the lower layer in the upper bulb to flow into the lower bulb and likewise rinse the upper bulb with a little ether-hydrochloric acid. To remove more of the metal chlorides from the ether in the upper bulb, again add 10 c.c. of ether-hydrochloric acid solution *B*, shake and remove the bottom layers in each bulb by the same operations as before. After the two layers have separated in each bulb, add the lower layer in the bottom bulb to the contents of the porcelain dish and allow the lower layer in the upper bulb to drain into the lower bulb. To be on the safe side, repeat this treatment with 10 c.c. of ether-hydrochloric acid solution *B* a third and fourth time. Then, as a rule, the separation is as complete as is necessary and it may be assumed that the solution in the porcelain dish now contains all the manganese, nickel, cobalt, chromium, aluminium, copper, titanium, sulfuric acid, phosphoric acid, and vanadium together with small quantities of iron.

Large amounts of alkali salts cause trouble; the ether causes them to precipitate and the deposited salts tend to clog the borings in the stopcocks. For this reason the use of alkali salts must be avoided in preparing a solution for treatment with ether. Thus oxidation must be accomplished with nitric acid rather than with potassium chlorate and any excess of acid removed by volatilization rather than by neutralization with ammonia.

In the apparatus, the iron is left as ferric chloride dissolved in ether and hydrochloric acid. By shaking with water, the greater part of the ether can be separated from the ferric chloride and the solution of the latter may be used for the determination of iron (see Iron). When the method is used frequently, it is well

to recover the ether. After washing it with sodium hydroxide solution, and drying over calcium chloride, it can be easily distilled from a steam bath. It is necessary to keep all gas flames away from the vicinity of the distilling apparatus on account of the danger of the vapors taking fire.

Drive off the ether from the hydrochloric acid extract containing the manganese and other metals by heating the porcelain dish at one of the cooler places on the steam bath and then evaporate to dryness. Take up the residue in a little dilute hydrochloric acid, rinse the solution into a 100-c.c. beaker and precipitate any copper present by the addition of a few cubic centimeters of saturated hydrogen sulfide water, stirring with a glass rod until the copper sulfide precipitate collects together and settles. Then filter into the original porcelain dish, add a little sulfuric acid to the filtrate and evaporate to dryness. Dissolve the residue in a little dilute sulfuric acid and transfer the solution to a platinum dish of 11 to 13 cm. diameter (Fig. 14). The quantity of sulfuric acid used must be adjusted so that in the following evaporation all the chlorides present will be changed to sulfates and upon stronger ignition (on the Finkener tower) a slight excess will be evolved in fumes. After this treatment is accomplished, allow the dish to cool. It is now ready for the fusion.

Fusion with caustic soda serves to free the manganese (together with any nickel, cobalt and iron), from phosphoric acid, chromium, vanadium and aluminium.

According to the amount of sulfates present, dissolve from 2 to 5 g. of pure sodium hydroxide in a platinum crucible with as little water as possible, and add the solution to the contents of the platinum dish. The metal salts are at once decomposed by the alkali. Take hold of the dish in some such way as shown in Fig. 14, and carefully evaporate the solution to dryness by moving the dish back and forth over a small Bunsen flame. Too rapid evaporation will cause loss by spattering. Continue the heating till the solid melts but avoid overheating. When a quiet fusion is obtained, allow the mass to cool somewhat and sprinkle over the top a little potassium chlorate or sodium peroxide (a quantity such as can be held on the point of a penknife suffices). Turn up the Bunsen flame just a little and heat the

dish, while moving it about, until the entire contents are fused and no lumps of undecomposed sodium peroxide are visible.

Heating any part of the dish more strongly than is necessary to accomplish fusion must be avoided, as otherwise the platinum dish will be attacked. If care is exercised, however, this operation can be carried out with either potassium chlorate or sodium peroxide without the platinum dish being injured.

After cooling the fusion, remove the holders, cover the dish with a watch-glass and dissolve the contents by adding about 60 c.c. of hot water; any excess of sodium peroxide is decomposed by this treatment and oxygen is evolved. Treat the solution, which is usually colored green by manganate, with a little more sodium peroxide; this decomposes the manganate, forming manganese dioxide with evolution of oxygen.

To destroy the excess of sodium peroxide, heat the covered dish and its contents for half an hour on the steam bath. Then rinse into a 300 to 400-c.c. beaker, dilute with water to about 200 c.c. and allow the precipitate to settle. Usually a slight yellowish-brown stain remains in the platinum dish. Dissolve this with a little dilute sulfuric acid and a small crystal of oxalic acid but do not add this solution to the main solution at present.

In the analysis of most iron and steel samples, the solution above the manganese dioxide precipitate (which also contains nickel, cobalt and iron) is usually colored more or less yellow by a little chromium. Allow the solution to cool, and, without stirring up the precipitate, decant the clear, supernatant liquid through 7 or 9 cm. filter, according to the size of the precipitate. Add hot water to the precipitate, allow it to settle and again decant. Repeat this operation once or twice more, and place a fresh beaker, or Erlenmeyer flask, under the funnel. Then, if subsequent washings run through the filter turbid, it will not be necessary to refilter the entire solution. Transfer the precipitate to the filter and wash it carefully. When the alkali salts are all removed there is danger of some of the precipitate becoming colloidal and passing through the filter. This may be avoided, if toward the end of the washing a dilute solution of ammonium sulfate is used instead of pure water, or if from time to time a small crystal of ammonium sulfate is placed in the filter and the washing done with pure water.

The combined filtrate contains all the chromium and aluminium besides the phosphorus and vanadium. It can be used for the determination of these elements.

Upon the filter are the hydrated oxides of manganese, nickel and cobalt together with a little iron that remained in the aqueous solution after treatment with ether. Dissolve the precipitate in a little concentrated hydrochloric acid. If there is much precipitate, wash as much as possible into a small beaker, place the beaker under the funnel and dissolve the precipitate by pouring strong hydrochloric acid through the filter; if there is only a little precipitate, place the beaker at once under the funnel and dissolve all the precipitate on the filter. Wash the filter thoroughly with hot, dilute hydrochloric acid. Add to the solution the sulfuric and oxalic acid solution that was previously obtained by dissolving the stain on the platinum dish. Evaporate on the steam bath to remove free chlorine and until the volume of liquid is small; the color of the solution may be yellow from a little dissolved ferric chloride, or more or less yellowish green if nickel is present.

When much nickel is present, the treatment of the solution, after the removal of the greater part of the iron by shaking with ether, should be carried out as described on page 85.

To remove, now, small quantities of iron that escaped solution in ether (when the operation was properly carried out this should amount to only a few milligrams) nearly neutralize the free acid by the addition of ammonia but do not continue adding ammonia until a permanent precipitate is formed. To the barely acid solution, add 1 or 2 c.c. of 20 per cent ammonium acetate solution and heat just to boiling. Filter off the reddish-brown flocks of basic ferric acetate through a small filter and wash well with hot water. If the precipitate is at all bulky, dissolve it in hydrochloric acid and repeat the basic acetate separation exactly as before.

Combine the filtrates from the basic acetate precipitation, make slightly acid with acetic acid and saturate the cold solution with hydrogen sulfide gas. Without interrupting the current of hydrogen sulfide, slowly heat the solution to boiling, then turn out the flame and allow the solution to cool while hydrogen sulfide is constantly passing through it. After the precipitated

nickel and cobalt sulfides have settled, filter and wash carefully with water. Concentrate the filtrate in a porcelain dish; often during this evaporation some more nickel sulfide precipitates out. Transfer the solution to a beaker and once more introduce hydrogen sulfide. After filtering off any nickel sulfide that may have formed, evaporate to expel hydrogen sulfide.

Transfer the solution containing the manganese to a 400-c.c. beaker, dilute to about 200 c.c. and neutralize with ammonia. Add a little bromine water and a slight excess of ammonia. Heat the liquid and stir to facilitate the formation of the manganese dioxide precipitate. By adding more bromine and making slightly ammoniacal again, make sure that the precipitation of the manganese was complete. In case an appreciable quantity of precipitate was formed the last time, repeat the operation.

After allowing to stand a short time on the water bath, filter the liquid through an ashless paper and wash the precipitate a few times with hot water. Test the filtrate for manganese by treatment with bromine and ammonia and, in case no precipitate forms, evaporate the liquid to dryness, which sometimes causes the deposition of small quantities of manganese dioxide.[1]

It is a quite common practice among chemists to ignite and weigh this precipitate, calling it Mn_3O_4. According to the quantity of precipitate and the ignition temperature, however, the

[1] In a dilute acid solution bromine has scarcely any oxidizing effect upon manganous ions. In other words the reaction:

$$Mn^{++} + Br_2 + 2H_2O \rightleftarrows MnO_2 + 2Br^+ + 4H^+$$

reaches an equilibrium before little, if any, of the manganese is precipitated. On the other hand, when the acid is neutralized the equilibrium of the above reaction is disturbed and the precipitation of the manganese as dioxide may be made quantitative. Ammonia is used in the above test as a neutralizing agent. Bromine, however, also reacts directly with ammonia and oxidizes a part of its nitrogen to free nitrogen in the sense of the following equation:

$$8NH_3 + 3Br_2 = 6NH_4Br + N_2$$

This reaction often goes a little farther and part of the ammonium salt is oxidized, leaving the solution slightly acid;

$$2NH_4^+ + 3Br_2 \rightleftarrows N_2 + 6Br^- + 8H^+$$

Although this last reaction takes place only to a slight extent, it is clear that, as a result of the two last reactions, the precipitation of the manganese is made more difficult. This is the reason for the repeated treatment with bromine and ammonia.

oxygen content varies somewhat so that it is better to convert it into either pyrophosphate or sulfate. In either of the latter forms, the composition of the ignited precipitate is constant and the results obtained are exact.

To convert the manganese dioxide precipitate into pyrophosphate, dissolve it in hot, dilute hydrochloric acid to which a few cubic centimeters of sulfurous acid have been added. Pour the acid through the filter and wash the latter thoroughly with hot water. Dilute the solution to 100 c.c., add 20 g. of ammonium chloride, 5 to 10 c.c. of a cold, saturated solution of disodium phosphate and ammonia, drop by drop, until a slight excess is present. Heat to boiling and keep at this temperature for 3 or 4 min., or until the precipitate assumes a silky crystalline appearance. Allow the solution to cool.

When a precipitate can be dried easily and completely at a temperature not far from the boiling point of water, it used to be common practice to filter it upon a weighed (*tared*) filter. Gooch, however, proposed the use of a perforated crucible containing a felt of asbestos fibers to serve as filtering medium. This has two advantages: first, the crucible may be dried at a temperature much higher than could be used with a paper filter; second, suction can be used during filtration and considerable time saved. If the asbestos felt is properly prepared and the crucible is dried originally to constant weight at the temperature to which the precipitate is to be heated, the results are as good as those obtained by any other method.

To prepare the asbestos felt, first digest the asbestos fibers, in pieces about 0.5 cm. long, for about an hour on the water bath with strong hydrochloric acid. Collect the asbestos upon a filter plate and wash out all the acid with water. Shake it up in a bottle with water so that a thin suspension is formed. Stretch a piece of "bill-tie" rubber tubing over a funnel, Fig. 15, and place the crucible, *T*, in the opening.[1] The funnel should

[1] Instead of using the flat rubber band to support the crucible, L. H. Bailey has devised a Gooch crucible holder which is shown in Fig. 16. It is made of rubber and fits an ordinary 2-in. glass funnel. The funnel is inserted in a perforated rubber stopper which in turn fits the suction flask. The upper edge of the holder projects over the upper edge of the funnel and the lower edge of the holder rests on the side of the funnel. When suction is applied the holder fits tightly to the funnel.

be large enough so that the crucible is suspended by the rubber without touching the sides of the funnel. Pour enough of the asbestos suspension into the crucible, applying gentle suction, to produce a layer 1 or 2 mm. thick. Place a small filter plate upon this layer and pour a little more asbestos into the crucible. Pour water through the crucible until no more asbestos fibers are washed away. To see the fibers, pour the liquid into a small beaker and hold it up to the light.

FIG. 15.

FIG. 16.—Sectional view of Bailey's Gooch crucible holder with funnel and crucible.

Instead of using an asbestos felt, Munroe,[1] Neubauer and others have recommended the use of platinum sponge. To prepare such a felt, place the perforated crucible upon several layers of filter paper and pour into it a mixture of ammonium chloroplatinate crystals ground up with a little alcohol. Heat the crucible carefully and shape the felt to the bottom of the crucible, finally burnishing it slightly with the aid of a glass rod of suitable shape.

The manganese ammonium phosphate precipitate may be filtered off through a washed filter, ignited carefully in a

[1] MUNROE, C. E., *J. anal. Chem.*, **2**, 241; *Chem. News*, **58**, 101; SNELLING, W. O., *J. Am. Chem. Soc.*, **31**, 456 and SWETT, O. D., *Ibid.*, **31**, 928. The last reference gives a table of suitable solvents for removing ignited precipitates.

porcelain crucible and weighed as manganese pyrophosphate. It is fully as satisfactory, however, to use either the Gooch or Munroe crucible. First, dry the crucible ½ hr. at about 130° and then ignite it in an electric furnace, or within a larger crucible heated by a gas flame. In this way there is no danger of gases from the flame coming in contact with the asbestos or platinum felt. After igniting at a high temperature for about 10 min., allow the crucible to cool in the air somewhat[1] and then let it remain half an hour in a desiccator before weighing.

Filter off the manganese ammonium phosphate using either the weighed Munroe or Gooch crucible, and wash the precipitate thoroughly with a cold, 10 per cent, solution of ammonium nitrate. Dry the crucible and its contents for at least ½ hr. at about 130° and then gradually raise the temperature until finally a high heat is obtained. Duringt his last heating the manganese ammonium phosphate is changed to manganese pyrophosphate:

$$2MnNH_4PO_4 = Mn_2P_2O_7 + 2NH_3 + H_2O$$

It is very important not to ignite the precipitate too quickly, as in that case the ammonia acts upon the phosphate, reducing it and turning it black; it is a tedious operation to whiten such a precipitate by ignition.

To convert the manganese dioxide precipitate into sulfate, ignite it with the filter in a weighed porcelain crucible, cover the crucible with a watch-glass, and dissolve the precipitate in hydrochloric acid (d. 1.12). Heat carefully until the chlorine is expelled and add, for each 0.1 g. of precipitate, about 0.5 c.c. of dilute sulfuric acid (1:5). To remove the excess of the latter, heat the crucible and its contents in an air bath, which may be prepared according to the suggestion of Gooch and Austin,[2] with the aid of a larger porcelain crucible.[3] The outer crucible

[1] If the very hot crucible is placed immediately in a desiccator with a tightly fitting cover, the expansion of the air causes the top of the desiccator to jump up and down several times and then, on cooling, a partial vacuum is produced in the desiccator. As a result the crucible cools very slowly. If weighed while still warm, it will weigh too little, owing to air currents rising from the balance pan. Much time is saved, therefore, by allowing the crucible to cool somewhat before placing it in the desiccator.

[2] *Z. anorg. Chem.*, **17**, 264 (1898).

[3] If an electrically-heated drying oven is available, heat the crucible in it to constant weight at 450 to 500°.

(Fig. 17), is chosen of such a size that when the smaller crucible is placed within it, and suspended by a piece of asbestos cord wrapped around it, or by means of a small triangle, the distance between the walls of the two crucibles is about 1 cm. on all sides.

Heat the outer crucible for a short time with a good Bunsen flame, cool and weigh. Continue the heating until a constant weight is obtained. The manganese sulfate should be pale pink, not brown at the bottom, and should be perfectly soluble in water.

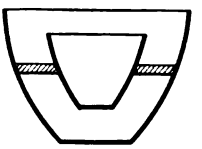

FIG. 17.

Computation.—If p_1 is the weight of manganese pyrophosphate and s the weight of substance taken, then

$$\frac{2\text{Mn} \times p_1 \times 100}{\text{Mn}_2\text{P}_2\text{O}_7 \times s} = \frac{38.70p_1}{s} = \text{per cent Mn}$$

If p_2 is the weight of the manganese sulfate and s the weight of substance taken, then

$$\frac{\text{Mn} \times p_2 \times 100}{\text{MnSO}_4 \times s} = \frac{36.38p_2}{s} = \text{per cent Mn}$$

The method can be modified to advantage in the analysis of special materials:

(*a*) *Alloys Rich in Manganese.*—(Ferro-manganese, metallic manganese, etc., which contain only little iron). Dissolve from 2 to 4 g. of metal[1] in nitric acid, decompose the nitrates and remove the silica[2] as described previously. Carefully add ammonia to the filtrate from the silica until the solution is neutral, add ammonium acetate, and carry out a basic acetate separation (*cf.* p. 78). If there is a considerable precipitate of basic ferric acetate, redissolve it and repeat the precipitation. Make the entire filtrate slightly acid with acetic acid and precipitate the copper, nickel and cobalt with hydrogen sulfide. Transfer the filtrate to a calibrated 250-c.c. flask, when it is at the laboratory temperature, make up to the mark and thoroughly mix by pouring back and forth several times into a dry beaker. By

[1] As regards the necessity for getting a representative sample, see Part II of this book.

[2] In the dehydration of the silicic acid, the dish should not be overheated or there is danger of losing some manganous chloride by volatilization.

means of a 50-c.c. pipette, take an aliquot part for the manganese determination.[1]

The determination of the manganese can now be carried out in the same way as before. In some cases, however, calcium is likely to be present and then the manganese dioxide precipitate will contain some of this element.[2] It is better, then, to precipitate the maganese as sulfide by passing hydrogen sulfide into the slightly ammoniacal solution. The manganese sulfide is easily converted into sulfate (*cf.* p. 48).

(*b*) *Alloys Rich in Nickel.*—(Nickel steel with high nickel content, chrome-nickel steel, etc.). To avoid the difficulties involved in precipitating considerable nickel in the presence of

[1] To avoid error in taking the aliquot part, it is necessary to make sure that the pipette and calibrated flask are properly calibrated. This is particularly necessary because several temperatures have been suggested as standards for calibration purposes and, moreover, both flasks and pipettes are calibrated in two ways—for contents and for delivery. In this case, the flask should be calibrated for contents and the pipette for delivery. A simple way to test the flask is to take some water that is at the room temperature and add the contents of the 50-c.c. pipette five times to the dry flask. In using the pipette, allow the pipette to flow freely and when the liquid stops flowing, touch the sides of the flask, or the surface of the liquid, with the point of the pipette to remove another drop, and then take away the pipette (do not blow through it). Place a mark on the neck of the flask where the bottom of the meniscus comes. It is best to dry the flask again and repeat the operation. It makes no difference now, whether the 250-c.c. flask or the pipette has been correctly calibrated because it is known that the pipette will deliver exactly one-fifth of the solution in the flask. It is important, however, to make sure that the solution has the same temperature when made up to the mark that it has when the aliquot part is taken. If the solution is warm when made up to the mark and cools during the pouring back and forth into the beaker, then the results will come out too high and conversely.

If there is a balance in the laboratory capable of weighing 1 kg. and sensitive to a centigram, it is more accurate to use it for dividing the solution. Weigh the perfectly dry flask, together with its ground glass stopper, and then weigh it again with the solution in it, without taking special pains to bring it exactly to any specified volume. Thoroughly mix the solution and pour a part of it into another weighed flask. Stopper this flask and again weigh it. From the ratio between the two weights of the solution the corresponding fraction of the weight of sample taken for analysis can be computed.

[2] *cf.* Reis, *Z. angew. Chem.*, **1892**, 672.

manganese, due to the fact that the solubility products of nickel and manganese sulfides lie comparatively near together, it is better to remove most of the nickel, after shaking out the ferric chloride with ether, in the following manner: Evaporate the hydrochloric acid solution to dryness, taking care not to set fire to the ether it contains, take up the residue in hydrochloric acid and neutralize the excess of acid with ammonia. Add bromine, make slightly ammoniacal again and heat. By this treatment, the greater part of the nickel remains in solution forming a blue liquid, and the manganese together with the remainder of the iron and some nickel is contained in the precipitate. Filter off the brown precipitate and again test the filtrate for manganese by treatment with bromine and ammonia. Dissolve the precipitated oxides on the filter by treating with hydrochloric acid[1] (d. 1.12), add a little sulfuric acid, and evaporate the solution on the Finkener tower until fumes of sulfuric acid are evolved. Fuse the residue with sodium hydroxide and either sodium peroxide or potassium chlorate and thus remove the remainder of the iron and nickel by the method described on p. 78. Eventually determine the manganese as sulfate or pyrophosphate.[2]

(*c*) *Materials Insoluble in Acid.*—(Ferro-chrome, ferro-tungsten, silico-manganese, etc.).

Such materials can be attacked by the ignition method described in the chapter on Silicon. It is usually advantageous to use the sodium carbonate and magnesia mixture in the proportions suggested by Rothe.

Weigh out from 0.5 to 2 g. of substance, according to the probable manganese content, ignite it with sodium carbonate and magnesia, transfer the ignited mass to an agate mortar, moisten it with water and rub it up with the pestle to as thin a paste as possible. Rinse into a beaker, dilute with hot water to a volume of about 200 c.c. and reduce the manganate by adding a little sodium peroxide. After destroying the excess of peroxide by boiling the liquid, allow the precipitate to settle, decant off

[1] If the precipitate remains on the filter very long, it may be necessary to add a little sulfurous acid to the hydrochloric acid.

[2] If phosphorus and manganese are not present to an appreciable extent, the fusion with sodium hydroxide and peroxide may be omitted. The iron and nickel are then removed in the usual way.

the supernatant liquid through a filter and wash several times by decantation, taking pains to keep the precipitate off the filter as far as possible.

Finally, dissolve the washed precipitate in the beaker by the addition of hydrochloric acid (d. 1.12), add to the solution the filter with the small deposit of manganese dioxide upon it, and heat to expel chlorine. Filter off the filter paper shreds and any unattacked material and wash the filter with water containing hydrochloric acid. If some unattacked material is found (this usually collects in the bottom of the beaker in the form of small black particles, having a gritty feeling when pressed upon with a glass stirring-rod) burn the filter in a platinum dish and fuse the ash with sodium carbonate. Take up the product of the fusion with water and add sodium peroxide to reduce the manganate, if any is shown to be present by the green color of the aqueous extract. Filter off the precipitate of manganese and ferric oxides, etc., add the filtrate to that obtained from the fusion with sodium carbonate and magnesia, and add the hydrochloric acid solution of the precipitate to the main hydrochloric acid solution.

The alkaline solution thus obtained may be used for the determination of phosphorus or chromium.

Evaporate the hydrochloric acid solution of the precipitate containing the manganese to dryness in a porcelain dish and heat for some time to 135° over an asbestos plate. After cooling, take up in hydrochloric acid and remove the silica as described on p. 64.

Dilute the filtrate from the silica to about 250 c.c., neutralize the free acid by the addition of ammonia, add ammonium acetate and precipitate the iron as basic ferric acetate, as described on p. 78. Usually it is advisable to carry out a second basic acetate separation.

Make the filtrate distinctly acid with acetic acid and introduce hydrogen sulfide to precipitate any nickel present. Filter off the nickel sulfide, catching the filtrate in a 300-c.c. beaker, and precipitate the manganese by the addition of bromine and ammonia (*cf.* p. 79). The precipitation may be hastened by vigorous stirring.

Filter off the precipitate, wash it well with water, and preserve the filtrate in order to test it for manganese. Transfer,

by means of a stream from the wash bottle, as much as possible of the precipitate to a beaker, place the beaker under the funnel and pour hydrochloric acid (d. 1.12) through the filter. Wash the filter thoroughly and heat the acid to dissolve the manganese dioxide. Concentrate the solution until the volume is very small and precipitate the manganese as sulfide, using freshly prepared ammonium sulfide[1] as reagent.

To carry out the precipitation, take 50 to 100 c.c. of ammonium sulfide solution (according to the quantity of manganese present), and heat it just to boiling in a 300 to 400-c.c. beaker. Heat the manganese solution, which must be as nearly neutral as possible, and pour it into the hot ammonium sulfide solution. Rinse out the beaker that contained the manganese solution and heat the liquid a short time in order to obtain a precipitate of green manganese sulfide that will filter well.

After allowing all the precipitate to settle, pour the liquid through a filter that runs well[2] and wash the precipitate with hot water containing a little ammonium sulfide. Evaporate the filtrate and washings and recover any manganese that it may contain by treatment with bromine and ammonia. This treatment with bromine and ammonia should be repeated to be sure that all manganese has been precipitated.

Ignite the manganese sulfide precipitate in a weighed porcelain crucible, dissolve the resulting manganomanganic oxide in hydrochloric acid (d. 1.12) and convert it into the anhydrous sulfate as described on p. 82. The small quantity of manganese dioxide recovered from the filtrates may be ignited separately and weighed as Mn_3O_4.

[1] To prepare ammonium sulfide free from polysulfide, saturate ammonia water (d. 0.96) with hydrogen sulfide and then add an equal volume of ammonia water.

[2] If the precipitate at first runs through the filter, continue to filter (provided the liquid does not run too slowly through the filter), and eventually transfer all the precipitate to the paper. As soon as the filtrate begins to run through clear, change the vessel under the funnel and pour the turbid filtrate through the filter again. In filtering keep the filter nearly filled all the time and do not wait for all the liquid to run through during the washing. Otherwise, the manganese sulfide oxidizes on the filter, dissolves in the wash water, and a precipitate of manganese sulfide is formed again in the filtrate which contains ammonium sulfide.

Short Gravimetric Method.—The time required for determining manganese gravimetrically may be shortened considerably up to the point of the ether separation, by using a round-bottomed flask instead of porcelain casserole for dissolving the sample. For samples weighing from 5 to 10 g., a flask of about 500-c.c. capacity is suitable, or a 300-c.c. flask for a 3-g. sample.

Weigh the sample directly into the flask, dissolve it by the gradual addition of the necessary quantity of nitric acid (d. 1.18) heat over a small flame until solution is complete, and evaporate over a free flame while keeping the flask in constant motion. Hold the flask by a clamp attached to the neck.

When the solution has evaporated to dryness, heat carefully to decompose the nitrates, allow to cool, dissolve the oxides in the necessary quantity of concentrated hydrochloric acid (d. 1.2) again evaporate to dryness, and continue the heating until the color of the residue is dark brown but not necessarily until it becomes red. Cool, dissolve in concentrated hydrochloric acid and heat until there is no ferric oxide visible in the bottom of the flask. Dilute and filter off the silica. Transfer the solution to the flask again and evaporate until it is ready for treatment with ether.

This method of working is not suitable when it is desired to determine the silicon because it is difficult to remove the last traces of silica from the flask.

Test Analyses.—To test the method described for the separation of manganese from iron, 25 c.c. of a manganous chloride solution, containing 0.0354 g. of manganese, were mixed with pure ferric chloride solution, corresponding to about 3.5 g. of iron, and the manganese determined. The average of three closely agreeing analyses gave 0.0364 g. of manganese when weighed as Mn_2O_4 and 0.0354 g. of manganese when weighed as $MnSO_4$.

Accuracy of the Results and Permissible Deviation

Besides errors in weighing, certain other unavoidable errors arise which in careful work should not be large. In general, if the manganese is weighed as sulfate or as pyrophosphate, the weight of the final precipitate should be accurate within 1 mg. when the precipitate weighs 50 mg. or less and within 2 mg. with

larger quantities. According to the amount of material taken for analysis (*e.g.*, 5 g. when less than 2 per cent of manganese is present and 1 g. otherwise) this will correspond to the following permissible deviations in duplicate results:

From	To	Deviation
0.0 per cent	0.2 per cent.....	± 0.01 per cent
0.2 per cent	1.0 per cent.....	± 0.02 per cent
1.0 per cent	5.0 per cent.....	± 0.04 per cent
5.0 per cent	10.0 per cent.....	± 0.06 per cent
10.0 per cent	30.0 per cent.....	± 0.08 per cent
30.0 per cent	upward.....	± 0.10 per cent

Applicability of the Gravimetric Method.—Satisfactory results are obtained in the analysis of iron, steel, and other alloys pertaining to the steel industry.

CHAPTER IV

PHOSPHORUS

Phosphorus, in varying quantities, is found in all kinds of iron and steel as well as in the various alloys used in steel making. Sometimes for special purposes, iron-phosphorus alloys are prepared containing as much as 25 per cent of phosphorus. In materials low in phosphorus it is present in solid solution with the iron but in materials rich in phosphorus (over 1.7 per cent P) it is also present in the form of free phosphide of iron.

As phosphorus shows a marked tendency toward segregation, it is necessary to exercise particular pains in selecting the sample for analysis.

All methods for the quantitative determination of phosphorus in iron and steel are based upon the preliminary oxidation of the phosphorus to phosphoric acid. Practically all phosphates, with the exception of sodium, potassium and ammonium phosphates, are insoluble in water but the phosphoric acid obtained in the chemical examination of iron and steel is usually precipitated either as ferric phosphate, ammonium phosphomolybdate or as magnesium ammonium phosphate.

The gravimetric methods are based upon the separation of the phosphoric acid from at least the greater part of the iron by precipitation as ammonium phosphomolybdate or as ferric phosphate; in the latter case, the greater part of the iron is kept in the ferrous condition and separated from a small part of the iron and all the phosphorus by the *basic acetate* method, according to which a precipitate of ferric phosphate and basic ferric acetate is formed. The ammonium phosphomolybdate, often called "yellow precipitate," is sometimes weighed as such or it may be dissolved in ammonium hydroxide solution and the phosphorus precipitated as magnesium ammonium phosphate which, by ignition, is easily changed to magnesium pyrophosphate. In the basic acetate method, the precipitate containing all of the phosphorus as ferric phosphate is dissolved in hydrochloric acid,

enough tartaric acid is added so that insoluble ferric hydroxide or phosphate is not formed upon the addition of ammonium hydroxide and the phosphorus is then precipitated as magnesium ammonium phosphate. In all the well-known gravimetric methods, therefore, the phosphorus is weighed as ammonium phosphomolybdate or as magnesium pyrophosphate.

The best-known volumetric methods are based on the properties of ammonium phosphomolybdate. The molybdenum content of this precipitate is more than 37 times as great as that of the phosphorus; the precipitate when dried at 120° contains approximately 1.63 per cent of phosphorus. The volumetric methods are essentially volumetric ways of estimating molybdenum. They depend upon the fact that the molybdic acid in the yellow precipitate can be made to react with a definite quantity of standard caustic alkali solution or it may be reduced to a lower state of oxidation and be then oxidized back by a definite quantity of standard oxidizing agent.

Many years of experience have shown that the so-called "rapid methods" are just as accurate as the longer methods when properly carried out but they are sensitive to slight changes in the conditions such as proper temperature, time allowed for the completion of the reaction, concentration and acidity. In the methods described first, it will be assumed that the original material is sufficiently soluble in acid and that there is no interfering element present. The treatment of ferro-silicon, iron phosphide and alloy steels will be discussed later.

1. DETERMINATION OF PHOSPHORUS IN STEEL BY THE MOLYBDATE-MAGNESIA METHOD

Principle.—When iron or steel is dissolved in nitric acid (d. 1.21) a part of the phosphorus is converted into phosphoric acid but the remainder is left in solution in the form of less highly oxidized acids, such as phosphorous acid. In order that this phosphorus may be made to react with the ammonium molybdate, it is necessary to convert it into phosphoric acid by means of a more energetic oxidizing agent or by evaporating to dryness and baking the residue.

With regard to the completeness of the precipitation of phos-

phoric acid by means of ammonium molybdate solution, Hundeshagen[1] has emphasized the following facts:

1. Free hydrochloric and sulfuric acids, or too concentrated nitric acid, prevent the complete precipitation of the phosphoric acid.

2. Small quantities of free nitric acid and salts of monobasic acids (chlorides, bromides) have no harmful effect.

3. Ammonium nitrate has a marked accelerating effect upon the precipitation of ammonium phosphomolybdate.

Raising the temperature also hastens the formation of the precipitate but when the precipitation takes place in the cold, as recommended by Finkener, there is less danger of an excess of molybdic acid being thrown down; this is important in all cases where the precipitate itself is to be weighed or the molybdenum in it determined as a measure of the phosphorus content.

When arsenic, tungsten or vanadium is present, the process which is to be described first cannot be used without modification.

Solutions Required.—*Nitric Acid.*—Mix 1,000 c.c. of nitric acid, d. 1.42 and 1,200 c.c. of distilled water. The density of the diluted acid is 1.24 and it is approximately 7-normal. Nitric acid of this concentration is prescribed for dissolving the original sample. For washing the ammonium phosphomolybdate precipitate, use 2 per cent nitric acid (prepared by mixing 20 c.c. of nitric acid, d. 1.42 with 1,000 c.c. of distilled water). Since 1 c.c. of the original nitric acid contains approximately 1 g. of dissolved HNO_3 (1.42×69.8) the percentage by volume of diluted nitric acid is practically the same as the percentage by weight; this is not true of the other common acids.

Potassium Permanganate.—Dissolve 25 g. of permanganate in 1,000 c.c. of distilled water.

Ammonium Bisulfite.—Dissolve 30 g. of ammonium bisulfite in 1,000 c.c. of water or add 80 c.c. of 6-normal sulfurous acid to 40 c.c. of 6-normal ammonium hydroxide and dilute the mixture to 1,000 c.c.

Ammonium Hydroxide, with approximately 10 *per cent* NH_3. Mix 1,000 c.c. of concentrated ammonium hydroxide, d. 0.90, with 1,700 c.c. of distilled water. The diluted solution has a density

[1] *Z. anal. Chem.*, **28**, 141 (1889).

of 0.96 and contains 9.90 per cent NH_3 by weight; it is commonly called 10 per cent ammonia.[1]

Ammonium Molybdate.—Solution No. 1.—Place 100 g. of "85 per cent" molybdic acid in a beaker, mix it thoroughly with 240 c.c. of water and 140 c.c. of ammonium hydroxide, d. 0.90, filter and add 60 c.c. of concentrated nitric acid, d. 1.42, to the filtrate.

Solution No. 2.—Mix 400 c.c. of nitric acid, d. 1.42 and 960 c.c. of water.

When the solutions are cold, add solution No. 1 to solution No. 2 while stirring constantly; then add 0.1 g. of ammonium phosphate dissolved in 10 c.c. of distilled water, stir and let the solution stand at least 24 hr. before using.

The ammonium molybdate solution should be kept in a cool place and must always be filtered just before using. The solution works well when *freshly prepared.* After standing a few months it may become almost worthless as a precipitant.

Magnesia Mixture.—Dissolve 50 g. of anhydrous magnesium chloride or 110 g. of the crystallized salt and 125 g. of ammonium chloride in 750 c.c. of water and then add 150 c.c. of ammonium hydroxide d. 0.90. The presence of the ammonium chloride cuts down the ionization of ammonium hydroxide to such an extent that magnesium hydroxide is not precipitated.

Procedure.—Weigh 5 g. of steel into a 300-c.c. Erlenmeyer flask and dissolve in 75 c.c. of the nitric acid. Heat the resulting solution to boiling and, while boiling, add 12 c.c. of the strong permanganate solution. Continue boiling until manganese dioxide precipitates. Dissolve the precipitate by the addition of small portions of ammonium bisulfite solution, avoiding an excess. Boil the solution until it is clear and free from brown fumes, cool to 35°, add 100 c.c. of the ammonium molybdate solution at room temperature, let stand 1 min., shake or agitate for 3 min. and then filter on a 9-cm. paper filter. Wash the precipitate at least three times with 2 per cent nitric acid solution to free it from iron.

Treat the precipitate on the filter with the 10 per cent ammonium hydroxide solution, letting the solution run into a 100-c.c. beaker containing 10 c.c. of concentrated hydrochloric acid

[1] *Am. Soc. Testing Materials,* **1915,** 211.

and 0.5 g. of citric acid; add 30 c.c. of concentrated ammonia solution and then add 10 c.c. of the magnesia mixture very slowly while stirring vigorously. Set aside in a cool place for 2 hr., filter and wash with the 10 per cent ammonium hydroxide solution. Ignite in a porcelain crucible and weigh. To correct for impurity, dissolve the precipitate of magnesium pyrophosphate in 5 c.c. of 6-normal nitric acid and 20 c.c. of distilled water, filter and wash the residue with hot water. Ignite and weigh. The difference between the two weights represents the weight of pure magnesium pyrophosphate; it contains 27.84 per cent of phosphorus.

The reactions that take place in this analysis may be expressed by the following equations:.

$$3Fe_3P + 41HNO_3 \rightarrow 9Fe(NO_3)_3 + 14NO + 3H_3PO_4 + 16H_2O$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23NH_4OH \rightarrow (NH_4)_2HPO_4 + 12(NH_4)_2MoO_4 + 11H_2O$$

$$(NH_4)_2HPO_4 + MgCl_2 + NH_4OH \rightarrow MgNH_4PO_4 + 2NH_4Cl + H_2O$$

$$2MgNH_4PO_4 \rightarrow Mg_2P_2O_7 + 2NH_3 + H_2O$$

2. DETERMINATION OF PHOSPHORUS IN STEEL BY THE ALKALIMETRIC METHOD[1]

This method proposed by Hundeshagen and also by Manby was subsequently modified by J. O. Handy. It depends upon the fact that ammonium phosphomolybdate can be dissolved in a known volume of standard alkali solution and the excess of the latter determined by titration with standard nitric acid using phenolphthalein as indicator.

Solutions Required.—The nitric acid for dissolving the sample and that for washing the yellow precipitate, the potassium permanganate, the ammonium bisulfite and the ammonium molybdate solutions are all prepared exactly as in the previous method.

Potassium Nitrate, 1 per cent.—Dissolve 10 g. of the salt in 1,000 c.c. of water.

[1] *Am. Soc. Testing Materials*, **1915**, 214.

Phenolphthalein Indicator.—Dissolve 0.2 g. in 50 c.c. of 95 per cent ethyl alcohol and 50 c.c. of water.

Standard Sodium Hydroxide.—Dissolve 6.5 g. of pure sodium hydroxide in 1,000 c.c. of distilled water, add a slight excess of a 1 per cent solution of barium hydroxide, and decant off the clear solution after it has stood over night. Standardize the solution against a steel of known phosphorus content,[1] as determined by the molybdate-magnesia method, and adjust the concentration so that 1 c.c. = 0.01 per cent phosphorus on the basis of a 2-g. sample. Protect the solution from carbon dioxide by means of a soda-lime tube.

Standard Nitric Acid.—Mix 10 c.c. of nitric acid, d. 1.42, and 1,000 c.c. of distilled water. Titrate the solution against the standard sodium hydroxide and adjust the concentration, by adding distilled water, until the two solutions are equal.

Sodium hydroxide absorbs carbon dioxide from the atmosphere and, with phenolphthalein in the cold, one molecule of carbon dioxide neutralizes as much sodium hydroxide as one molecule of nitric acid. If the temperature of the solution is raised to the boiling point and an excess of acid is added, all the carbonic acid is expelled. Consequently it is essential in this method of analysis, to guard against the absorption of carbon dioxide as much as possible, to always titrate at the same temperature, and to carry out the standardization in exactly the same way that the analysis is made. It is possible to compute the results on the basis that one molecule of ammonium phosphomolybdate reacts with 23 molecules of sodium hydroxide (*cf.* p. 94 where the reaction is written with ammonium hydroxide) but it is better to standardize against a steel with known phosphorus content.

Procedure.—Dissolve 2.00 g. of steel in 50 c.c. of the nitric acid using a 300-c.c. Erlenmeyer flask. Heat the solution to boiling and, while boiling, add about 6 c.c. of the permanganate solution. Continue boiling until manganese dioxide precipitates and dissolve the precipitate by additions of the ammonium bisulfite solution. Boil until the solution is clear and free from brown fumes, cool to 80°, add 50 c.c. of the ammonium molybdate at room temperature, let stand 1 min., shake or agitate for 3 min., and filter on a 9 cm. filter. Wash the precipitate three times

[1] Bureau of Standards Steel No. 19(*a*) is recommended.

with the 2 per cent nitric acid to free it from iron and then with 1 per cent potassium nitrate solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate back to the original flask, add 20 c.c. of water free from carbon dioxide, 3 drops of phenolphthalein solution as indicator and an excess of standard sodium hydroxide solution. Insert a rubber stopper in the neck of the flask and shake vigorously until all the precipitate dissolves. Wash off the stopper, rinse the sides of the flask with distilled water and determine the excess of sodium hydroxide by titration with standard nitric acid solution.

Computation.—If the two standard solutions are exactly the recommended strength, the per cent phosphorus is found by subtracting the volume of nitric acid used from the total volume of sodium hydroxide solution and moving the decimal point two places to the left. If both solutions are exactly tenth-normal,

$$\text{Per cent } P = \frac{(\text{c.c. NaOH} - \text{c.c. } HNO_3) \times 0.01348}{\text{wt. of sample}}$$

3. DETERMINATION OF PHOSPHORUS IN CAST IRON[1]

The determination of phosphorus in cast iron often causes trouble, particularly when titanium is present. The solutions required in this method of analysis are the same as given under the two methods already described.

Procedure for Non-titaniferous Irons.—Weigh 1.00 of the iron, or twice as much if the metal is low in phosphorus, into a 400-c.c. beaker and dissolve in 25 (or 50) c.c. of nitric acid. Evaporate to dryness and heat on the hot plate, or in an air bath, at approximately 200° for about an hour. This baking of the ferric nitrate accomplishes the same effect as the addition of permanganate in the analysis of steel by the preceding methods. Allow the beaker to cool and heat with 15 c.c. of concentrated hydrochloric acid until the iron oxide has all dissolved and then evaporate to dryness to render the silica insoluble. Redissolve in 15 c.c. of concentrated hydrochloric acid, dilute with water, filter off the insoluble silicious residue and wash the filter several times with dilute hydrochloric acid and then with water.

[1] *Am. Soc. Testing Materials*, 1915, 525.

This residue often contains a little phosphorus. To recover it, burn off the filter paper and the graphite by heating in a platinum crucible. Cool, add a few cubic centimeters of hydrofluoric acid and a drop of sulfuric acid and evaporate off all the silicon fluoride and excess hydrofluoric acid but stop heating before all the sulfuric acid is expelled. Take up the residue in a little concentrated hydrochloric acid, dilute and filter into the original solution.

Evaporate now to a small volume until salts just begin to separate. Add 10 c.c. of concentrated nitric acid and again evaporate to small volume, add 15 c.c. more of concentrated nitric acid and once more evaporate. Then, with the solution in an Erlenmeyer flask at a volume of not more than 25 c.c., add 25 to 100 c.c. of ammonium molybdate reagent, according to the phosphorus content. Shake the solution for 4 or 5 min. and allow the contents of the flask to stand for 30 min. (but not more than 4 hr.) at room temperature.

Three methods of treating the ammonium phosphomolybdate precipitate are recommended by the American Society of Testing Materials, either one of which should give good results.

(*a*) Filter into a weighed Gooch crucible, wash the precipitate once or twice with ammonium molybdate reagent diluted with an equal volume of water and then with 1 per cent nitric acid four times. Dry 1 hr. at 120° and assume that the precipitate contains 1.63 per cent phosphorus.

(*b*) Filter the solution through a 9-cm. paper filter and determine the phosphorus by the alkalimetric method described on page 94.

(*c*) Filter the solution through a small paper filter and determine the phosphorus as described on page 91.

Basic Acetate Procedure for Irons Containing Titanium.—The method of treatment is the same as recommended for the analysis of nontitaniferous irons down to the point where the residue from hydrofluoric acid treatment is dissolved and added to the main solution. After this has been done, heat the entire solution to boiling and add gradually from a small beaker a mixture of 2 c.c. ammonium acid sulfite solution (made by saturating concentrated ammonia solution with sulfur dioxide gas) and 10 c.c. of strong ammonia. The precipitate which forms at first, redissolves. If

at any time while adding the sulfite solution the precipitate will not dissolve, even upon stirring vigorously, add a few drops of hydrochloric acid and, after the solution clears, continue the addition, very slowly, of the ammonium acid sulfite solution. When all but a little of the reagent has been added, replace the beaker over the flame. Finally add to the hot solution ammonium hydroxide, drop by drop, until the solution is quite decolorized and a little more ammonia causes a slight greenish precipitate to remain undissolved even after stirring. Now add the remainder of the sulfite solution; this should throw down a white precipitate (titanium hydroxide) which usually redissolves leaving the solution quite clear and nearly colorless. If a precipitate remains, add hydrochloric acid, drop by drop, until the solution clears; it should smell perceptibly of sulfur dioxide.

If the solution of ammonium acid sulfite was too weak, the desired reduction of the ferric chloride will be incomplete and there will be no odor of sulfur dioxide on adding acid. In such a case add more acid ammonium sulfite (without the addition of ammonia) until the solution smells strongly of sulfur dioxide, then add ammonia solution until a slight permanent precipitate is formed and redissolve it in as little hydrochloric acid as possible.

At this point, the solution should be very nearly neutral, all of the iron should be in the ferrous condition and a slight excess of sulfurous acid should be present. Add 5 c.c. of concentrated hydrochloric acid to make it decidedly acid and to insure the complete decomposition of any excess ammonium sulfite that may be present. Boil the solution, while passing a stream of carbon dioxide through it, until every trace of sulfurous acid is expelled. (If arsenic is present, pass a current of hydrogen sulfide through the solution for 15 min., filter off the arsenic sulfide and expel the excess of precipitant while passing a current of carbon dioxide through the boiling liquid.)

The next step is to provide enough *ferric* ions to combine with all the phosphorus. This may be accomplished by adding a few drops of bromine water to the solution or by adding a little pure ferric chloride solution. After this has been done, cool the solution by placing the flask in cold water and slowly add ammonia solution, drop by drop at the last, with constant stirring. The green precipitate of ferrous hydroxide which is seen at first is

dissolved by stirring, leaving the solution clear. Subsequently, although the green precipitate redissolves, a whitish one of titanium hydroxide and ferric phosphate remains and the next drop gives a distinct reddish tint to the precipitate. Then, another of ammonia makes the whole precipitate appear green. If, before this occurs, the whole precipitate does not appear decidedly red in color, showing that a slight excess of ferric iron was present, dissolve the green precipitate with a drop or two of hydrochloric acid, add a little bromine water or 1 or 2 c.c. of dilute ferric chloride solution, and then treat with ammonia as before until a reddish precipitate is obtained before the green coloration appears. At this point the precipitate contains all the phosphorus as ferric phosphate together with a small amount of basic ferric salt and enough ferrous hydroxide to give a green color.

Dissolve the green ferrous precipitate by a few drops of acetic acid, sp. gr. 1.04, and the remaining precipitate should be distinctly red in color. Add about 1 c.c. of acetic acid in excess and dilute the solution with boiling water so that the 400-c.c. beaker is about four-fifths full. Boil the solution 1 min. and, while keeping the liquid hot, filter as rapidly as possible through a 14-cm. filter and wash once with hot water. The filtrate should run through clear at first but should become cloudy owing to the gradual oxidation of some of the ferrous salt which precipitates as basic ferric acetate.

Dry the precipitate on the filter without scorching the latter. Remove with filter paper any precipitate that may adhere to the beaker and dry this paper also. Transfer the main portion of the precipitate to a small porcelain mortar. Carefully burn the filter papers and transfer the ash to the mortar. Triturate the ferric phosphate and basic ferric acetate with 3 g. of anhydrous sodium carbonate and a little potassium nitrate. Transfer the mixture to a platinum crucible, cleaning mortar and pestle with a little more sodium carbonate, and fuse the mass for ½ hr. Cool, dissolve the fused mass in hot water, filter and wash with hot water. The residue on the filter will contain nearly all the titanium and the aqueous extract will contain all the phosphorus or sodium phosphate.

Acidify the alkaline solution with nitric acid, evaporate nearly to dryness in a small casserole, transfer to an Erlenmeyer flask

and, with the volume not more than 25 c.c., precipitate at room temperature with 25 to 100 c.c. of the molybdate reagent. From this point the procedure is the same as for non-titaniferous irons.

4. DETERMINATION OF PHOSPHORUS

BY METHOD OF C. M. JOHNSON[1]

All of the methods described thus far have called for the use of an acid solution of ammonium molybdate. Such a solution becomes turbid on standing and its precipitating power is continuously lessened. Johnson has found it advantageous to use a faintly ammoniacal solution of ammonium molybdate as reagent and has succeeded in modifying the conditions of precipitation so that the determination of phosphorus in materials containing vanadium is much easier than according to the methods formerly used.

The solutions required, except as indicated in the directions, are the same as recommended in the methods already described, with the exception of the ammonium molybdate reagent.

Ammonium Molybdate Solution.—Into each of four 800-c.c. beakers weigh 55 g. of ammonium molybdate and 50 g. of ammonium nitrate and add 40 c.c. of ammonium hydroxide, d. 0.96. Dilute the contents of each beaker with enough water to make the total volume 700 c.c. Heat for about 30 min. and stir occasionally until all the salts have dissolved. Combine the contents of the four beakers by pouring into a large bottle, dilute to 4,000 c.c. and allow to stand over night. Filter the next morning through double 15-cm. filters but do not wash the residue.

Procedure for Non-vanadium Steels and Cast Irons.—Weigh 1.63 g. of the iron or steel into a 150-c.c. beaker and dissolve in 45 c.c. of 25 per cent nitric acid, heating the contents of the beaker over a small flame. (If an insoluble residue remains filter it off and treat with HF, etc., as described in Method 3, finally concentrating the solution to 45 c.c.)

Add about 6 c.c. of strong permanganate solution and clear the solution as described in Methods 1 and 2. After boiling off the brown fumes, add 15 c.c. of concentrated nitric acid, rinse

[1] *J. I. E. C.*, **11**, 113 (1919).

down the cover glass and sides of the beaker and add 50 c.c. of ammonium molybdate reagent. Stir briskly (about 2 min.), until the precipitate is formed completely, allow to stand 20 min. and filter through a 7-cm. filter. Wash five times with 2 per cent nitric acid and then with 1 per cent potassium nitrate solution until the outside fold of the filter has no sour taste. With high phosphorus content this may take 35 or 40 washings. Continue the analysis as in Method 2.

If the steel contains 2.5 per cent vanadium or less, good results are obtained by practically the same procedure except that just before adding the ammonium molybdate, 40 to 50 c.c. of nitric acid are added instead of 15 c.c.

Procedure for Steels Containing More Than 2.5 Per Cent Vanadium.—Digest 1 g. of steel in a covered, 250-c.c. porcelain dish with a mixture of 30 c.c. concentrated hydrochloric acid and an equal volume of concentrated nitric acid. After heating about an hour, remove the cover glass, rinse off the bottom, and add 100 c.c. of concentrated nitric acid. Evaporate the solution to dryness and bake 5 min. at 200°. Cool, dissolve the oxides in 35 c.c. of concentrated hydrochloric acid, evaporate to 10 c.c., add 50 c.c. of concentrated nitric acid, again evaporate to 10 c.c., add 10 c.c. more of nitric acid and heat a short time with the dish covered. Filter through an asbestos pad on glass wool (*cf.* Volhard method for manganese) and catch the filtrate in a 150-c.c. beaker. Wash the vanadium oxide residue 15 times with small portions of a solution containing 200 c.c. of concentrated nitric acid, 100 c.c. of water and 20 g. of ferric nitrate free from phosphorus.

Concentrate the filtrate to 10 c.c. and filter off a second crop of vanadic acid anhydride. A third evaporation of the filtrate should show no further deposition of vanadic acid anhydride. Add 40 c.c. of concentrated nitric acid and 50 c.c. of ammonium molybdate. Filter, wash and analyze the precipitate as indicated above.

5. DETERMINATION OF PHOSPHORUS BY THE ACETATE METHOD OF A. A. BLAIR (MODIFIED)

The method is in principle the same as that recommended for the determination of phosphorus in cast irons containing titanium.

Procedure.—Dissolve 5 g. of borings in 80 c.c. of nitric acid (d. 1.2) and when the reaction begins to slacken add 10 c.c. of strong hydrochloric acid. Evaporate to dryness and bake until the nitrates are decomposed in order to oxidize all the phosphorus to phosphoric acid. Cool, add 30 c.c. of concentrated hydrochloric acid, heat until the ferric oxide has all dissolved and again evaporate to dryness but without baking the residue. Cool, dissolve in 30 c.c. strong hydrochloric acid, dilute and filter off the silica (*cf.* p. 104).

Dilute the filtrate from the silica to about 400 c.c. and add ammonia until a slight permanent precipitate of ferric hydroxide is formed. Add 200 c.c. of a saturated aqueous solution of sulfur dioxide and slowly heat to boiling. The precipitate soon dissolves and the liquid assumes a dark reddish brown color, which, on further heating, becomes light green or nearly colorless. As soon as this point is reached, add 10 to 20 c.c. of concentrated hydrochloric acid and introduce carbon dioxide gas until the excess of sulfur dioxide is expelled. Cool the solution by placing the beaker in cold water, add 1 or 2 c.c. of chlorine or bromine water to oxidize a little of the iron, and ammonia very carefully, with constant stirring, until the greenish precipitate of ferrous-ferric hydroxide dissolves with difficulty. Continue the addition of ammonia, drop by drop, until a distinct brown precipitate is formed which becomes green on stirring. If, before this occurs, the precipitate does not appear decidedly red in color, dissolve it with a drop or two of hydrochloric acid, add a little more chlorine or bromine water and repeat the addition of ammonia until a reddish brown precipitate is obtained and then the green coloration. Ferric phosphate being white, the formation of a red precipitate shows that there are more ferric ions present than are required to unite with all the phosphoric acid. Now add acetic acid (d. 1.04), drop by drop, until the green part of the precipitate redissolves leaving a reddish precipitate behind, add about 1 c.c. of acetic acid more, heat to boiling and keep at this temperature for 1 min. All the phosphorus is then precipitated as ferric phosphate and some of the iron is precipitated as basic ferric acetate, but the greater part of the iron remains in solution in the ferrous state Filter through a large filter and wash the precipitate once with hot

water. The filtrate is at first clear, but becomes turbid on standing in the air, owing to oxidation of the ferrous ions.

Dissolve the precipitate adhering to the sides of the beaker by warming it with about 15 c.c. of hydrochloric acid (1 vol. conc. acid: 1 vol. water) and add 10 c.c. of bromine water. If necessary, add a few drops more of concentrated hydrochloric acid to complete the solution of the precipitate. Pour the acid solution through the filter and catch the filtrate in a small beaker. Wash the filter well with hot water and evaporate the solution nearly to dryness to expel the excess of hydrochloric acid. Add a filtered solution of 5 or 10 g. of citric acid dissolved in 10 or 20 c.c. of water, also 10 c.c. of magnesia mixture[1] and enough ammonia to make the solution faintly alkaline. When perfectly cold, add one-half the liquid's volume of strong ammonia and stir well. After standing 12 hr., filter off the precipitate of magnesium ammonium phosphate and wash it with 2.5 per cent ammonia containing 2.5 g. of ammonium nitrate in 100 c.c. Dissolve the precipitate in hydrochloric acid, evaporate to dryness to remove silica obtained from the reagents and the glass, moisten the residue with a little hydrochloric acid, take up with a little water and filter through a small filter. To the filtrate, which should not be over 20 c.c. at the most, add 1 c.c. of the 50 per cent citric acid solution, 2 drops of magnesia mixture and reprecipitate the phosphorus in the same way as before. In this way a precipitate is obtained which yields pure magnesium pyrophosphate upon ignition.

Computation.—If p is the weight of ignited precipitate, and s the weight of sample taken, then

$$\frac{2P}{Mg_2P_2O_7}\cdot\frac{100}{s} = \frac{27.87p}{s} = \text{per cent P}$$

REMARKS.—Blair recommends the use of ammonium bisulfite instead of sulfurous acid for the reduction of the ferric salt. Commercial ammonium bisulfite sometimes contains phosphoric acid so that it seems safer to recommend sulfurous acid itself. Again, Blair suggests that hydrogen sulfide be passed into the solution after the excess of sulfur dioxide has been removed, in

[1] Dissolve 55 g. $MgCl_2.6H_2O$, and 70 g. NH_4Cl in water containing a little hydrochloric acid, add 250 c.c. of ammonia (d. 0.96), and dilute to 1 liter. Filter after the solution has stood several days.

order to precipitate any arsenic as the trisulfide. Unless this is done some arsenic is likely to be precipitated with the phosphorus. The filtrate from the hydrogen sulfide precipitation is heated to boiling, the excess of hydrogen sulfide expelled by means of a stream of carbon dioxide, and the solution then partly oxidized as described above.

If the material analyzed contains titanium, a compound containing titanic acid, ferric oxide and phosphoric acid is present in the insoluble residue obtained after evaporating the original solution to dryness. This residue should be filtered off, ignited and treated with sulfuric and hydrofluoric acids to remove the silica. After evaporating off the excess of sulfuric acid, fuse the residue with sodium carbonate and extract the fused mass with water. Acidify the aqueous solution with hydrochloric acid and add it to the main solution.

Another difficulty that is likely to be encountered when titanium is present, is the formation of the above-mentioned insoluble compound when the solution obtained by dissolving the acetate precipitate is being concentrated. To avoid this, the evaporation must be watched carefully and citric acid added as soon as any titanic acid begins to separate.

6. DETERMINATION OF PHOSPHORUS BY PERMANGANATE TITRATION

This method was recommended some years ago by a committee of American chemists consisting of W. P. Barba, A. A. Blair, T. M. Drown, C. B. Dudley and P. W. Shimer. It gives accurate results when the prescribed conditions are carefully maintained. It depends upon the precipitation of the phosphorus as ammonium phosphomolybdate under conditions such that the ratio of P:Mo = 1:12 is maintained, the dissolving of the precipitate in dilute ammonia, acidification with sulfuric acid, reduction of the molybdenum by zinc and titration back to the hexavalent condition by means of potassium permanganate.

Reagents Required.—Directions for preparing solutions of ammonium molybdate, 25 per cent nitric acid, 10 per cent ammonia solution, and strong permanganate were given in Methods 1 and 2. The other solutions required are:

Dilute Sulfuric Acid.—Add 25 c.c. of concentrated acid to 1 liter of water.

Acid Ammonium Sulfate.—To 1 liter of water add 15 c.c. of concentrated ammonia and 25 c.c. of concentrated sulfuric acid and stir well.

Standard Permanganate Solution.—Dissolve about 2 g. of potassium permanganate crystals for each liter of solution desired. In order that the solution may keep well, it is best to use the same care in preparing it as described on p. 57.

Any good method of standardizing a permanganate solution is perfectly satisfactory. It is a very common practice, however, to use metallic iron wire for this purpose; such a method will be described and it involves the use of the Jones reductor, which is also recommended for use in the phosphorus determination.

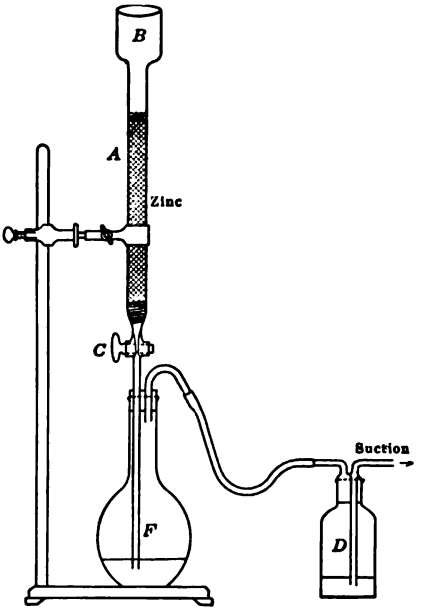

FIG. 18.

The Jones reductor, Fig. 18, consists of a glass tube *A* about 30 cm. long and with an inside diameter of about 18 mm.; at the bottom of the tube a piece of platinum gauze is placed or some glass beads. Then follows a plug of glass wool and a thin layer of asbestos such as is used for Gooch crucibles. The layer of asbestos on the glass wool should be somewhat less than 1 mm. in thickness. If too little asbestos is used, the zinc will pass through into the flask and cause trouble in the subsequent titration. Too thick a layer, on the other hand, soon becomes clogged and the liquid will pass through too slowly. The tube is finally filled with amalgamated zinc to within 5 cm. of the top and on the zinc is placed a little glass wool to act as a filter.

The amalgamated zinc is prepared by taking some granulated zinc which will pass through a 20-mesh sieve but not through a 30-mesh, cleaning it with a little hydrochloric acid and adding mercuric chloride solution until hydrogen ceases to be evolved.

Amalgamated zinc is just as efficient as pure zinc with regard to its reducing power upon ferric salts or upon molybdic acid but it does not dissolve readily in dilute sulfuric acid. For this reason the desired reduction can be accomplished by passing the solution through the tube which would be impossible with ordinary zinc on account of the lively evolution of hydrogen. Before using a Jones reductor after it has been standing for some time it should be washed well with dilute sulfuric acid.

In running a blank, *i.e.*, an experiment with the same quantities of acid and wash water as are to be used in the analysis or standardization,[1] and in all determinations, proceed as follows:

Pour 100 c.c. of hot, 2.5 per cent sulfuric acid into the funnel *B* which forms the top of the reduction tube, open the stopcock *C* and apply gentle suction. When only a little dilute acid remains in the funnel, add the solution to be reduced (50 c.c. of water, 10 c.c. of concentrated sulfuric acid and 5 c.c. of dilute ammonia in the case of blanks) and follow it with 250 c.c. of hot dilute sulfuric acid (with which the original beaker is washed in several portions) and 100 c.c. of water. Air should not be allowed to enter the reductor at any time by letting all the acid or water run out of the funnel, *B*. Before starting any analysis a blank should be run and the volume of permanganate required should not be over 0.2 c.c., as a rule. If more is required the blank test should be repeated.

Standardization of Permanganate Solution by Means of Iron Wire

Dissolve about 0.2 g. of standard wire in a 125-c.c. Erlenmeyer flask containing 30 c.c. of water and 10 c.c. of concentrated sulfuric acid. When the iron has all dissolved, boil the solution

[1] This is necessary on account of the iron, sulfur, etc., which the zinc contains. An allowance should be made for these impurities whenever zinc is used as a reducing agent.

gently for a few moments in order to expel hydrocarbons.[1] Pass the solution through the reductor, in the manner already described, and titrate slowly with the potassium permanganate solution. Duplicate results in a standardization should agree within 3 parts in one thousand. Greater precision is unnecessary in the analysis of iron or steel for phosphorus.

Analysis of Steel.—Weigh about 2 g. of borings into a 250-c.c. Erlenmeyer flask, add 100 c.c. of dilute nitric acid (d. 1.13) and insert a small funnel in the neck of the flask. Heat until the sample is all dissolved and the oxides of nitrogen are no longer visible in the flask. Add 10 c.c. of the strong permanganate solution, or more if necessary to impart a strong pink color to the solution. Boil until the pink color disappears and manganese dioxide is precipitated. Continue boiling for several minutes, then remove from the source of heat and add a few drops of sulfurous acid, a small crystal of ferrous sulfate, or a solution of 0.5 g. sodium thiosulfate in 10 c.c. of water, and repeat the addition of reducing agent at short intervals until all the manganese dioxide has dissolved.[2] Boil 2 min. longer and then cool by placing the flask in cold water or by allowing it to stand in the air until it feels cool to the hand. Add carefully 40 c.c. of dilute ammonia and rotate the flask until the precipitated ferric hydroxide all dissolves and a pale yellow solution is obtained. When the solution is at about 35° , add 40 c.c. of ammonium molybdate solution, close the flask with a rubber stopper and shake for 5 min. Allow the precipitate to settle for a few minutes and filter. Wash the precipitate several times by decantation and then on the filter with acid ammonium sulfate solution until 2 or 3 c.c. of the filtrate give no reaction for molybdenum when tested with yellow ammonium sulfide. It is best to compare the test with a blank made by adding some of the wash liquid itself to a drop of yellow ammonium sulphide solution. When iron is present a black precipitate is obtained while the test solution is still ammoniacal, but

[1] Many chemists oxidize the carbonaceous matter with strong permanganate, but this is hardly necessary with good iron wire as the error is not more than 2 parts in one thousand and this is far less than the error involved in the determination of small quantities of phosphorus.

[2] If there is considerable residue at this point the solution must be filtered.

with molybdenum the brown sulfide will not form until enough acid ammonium sulfate solution has been added to make the test acid.

Dissolve any of the precipitate remaining in the flask by means of 5 c.c. of strong ammonia diluted with 20 c.c. of water, and pour this through the filter. Wash out the flask and the filter until the volume of the solution amounts to 60 or 75 c.c. Add 10 c.c. of concentrated sulfuric acid and pass through the Jones reductor. The solution is preceded and followed by the same quantities of dilute sulfuric acid and water as in running a blank or a standardization. By adding the strong sulfuric acid to the ammoniacal solution, the latter is heated enough so that the molybdenum is reduced readily by the amalgamated zinc. The solution as it passes through the reductor should be bright green in color. Titrate with the standard permanganate solution, avoiding much shaking, until the permanganate color persists for 1 min. While adding the permanganate, the green color disappears, and the solution becomes brown, pinkish yellow and finally colorless before the end point is reached.

Computation.—The amalgamated zinc reduces the molybdenum from the hexavalent to the trivalent condition but there is a slight oxidation by the air in the flask. It is customary, therefore, to assumed that the molybdenum is in the state of oxidation corresponding to $Mo_{24}O_{37}$ when the permanganate titration is made, which requires the equivalent of 35 atoms of O, to oxidize the molybdenum to the state corresponding to $24MoO_3$. We have, then, $1P = 12\,MoO_3 = 35H$

$$1 \text{ c.c. of } NK.MnO_4 \text{ solution} = \frac{P}{35{,}000} = 0.0008857 \text{ g. P}$$

If 1 c.c of $KMnO_4$ solution will oxidize a g. of iron or b g. of pure sodium oxalate, then

$$1 \text{ c.c. } KMnO_4 = \frac{P}{35Fe} \times a \text{ or } \frac{2P}{35Na_2C_2O_4} \times b \text{ g. P}$$

From the actual burette readings, the volume of permanganate required for the blank must be deducted in both the analysis and in the standardization.

Ferric Alum Modification

Proceed exactly as in the preceding method up to the point of passing the sulfuric acid solution through the reductor. Instead of passing the reduced solution into an empty flask, place in the flask about 50 c.c. of ferric alum solution[1] and make sure that the tube from the reductor passes into the solution. In all other respects the two methods are identical. There is now no oxidation of the trivalent molybdenum by air in the flask but it is converted back to the hexavalent condition by means of the ferric salt and an equivalent amount of the latter is reduced to ferrous salt. In this case, therefore, the ferrous iron is really titrated by the permanganate but the volume of reagent required corresponds to the amount necessary to convert Mo_2O_3 to MoO_3. The computation is the same as before except that 1P = 36H.

7. DETERMINATION OF PHOSPHORUS IN MATERIALS INSOLUBLE IN NITRIC ACID

(Ferrosilicon, Iron Phosphide, etc., and Alloy Steels)

Materials insoluble in nitric acid are attacked best by ignition with a mixture of sodium carbonate and magnesia as described in the chapter on Silicon. Ignite from 1 to 3 g. of the finely pulverized material with six to eight times as much of the sodium carbonate-magnesia mixture (2 : 1).

After the ignition, dissolve the mass in hydrochloric acid and remove the silica in the usual manner. After volatilizing the silica as silicon tetrafluoride by treatment with sulfuric and hydrofluoric acids, fuse the residue with sodium carbonate, dissolve the product of the fusion in hydrochloric acid and examine the solution for phosphoric acid. Concentrate the filtrate from the silica precipitation (or an aliquot part of it if much phosphorus is present) as described on p. 97 and determine the phosphorus as ammonium phosphomolybdate.

Carry out a blank determination with the reagents used and

[1] Dissolve 100 g. of $Fe_2(SO_4)_3$, $(NH_4)_2SO_4$, $24H_2O$ in 1 liter of water and 25 c.c. of concentrated H_2SO_4 and add 40 c.c. of sirupy H_3PO_4. The amount of ferric alum solution used should be sufficient to react with all the reduced molybdenum. Blanks should be run, with the same volume of ferric alum in the flask.

deduct the weight of ammonium phosphomolybdate thus obtained from that obtained in the regular analysis.

In determining the phosphorus content of ferrotitanium and of metallic titanium, wash thoroughly with cold water the product of the ignition with sodium carbonate and magnesia, filter off the insoluble residue and fuse it with sodium carbonate to obtain any residual phosphorus. Extract this second melt with cold water and add the solution to that previously obtained; the residue will contain all the titanium as sodium titanate.[1] Acidify the aqueous extract with hydrochloric acid, evaporate to dryness in order to remove the silica and then determine the phosphorus in the filtrate by precipitation with ammonium molybdate.

8. DETERMINATION OF PHOSPHORUS IN MATERIALS CONTAINING ARSENIC

(Hydrobromic Acid Method)

Influence of Arsenic upon the Precipitation of Phosphorus.—The statements in the literature concerning the effect of arsenic upon the determination of phosphorus in iron and steel are conflicting. Ledebur states that an arsenic content of less than 0.1 per cent has no effect upon the determination but cites values which are 20 per cent too high in the case of ingot iron containing 0.37 per cent arsenic. On the other hand, Frank and Hinrichsen[2] state that the Finkener method for determining phosphorus gives values ranging up to 0.015 per cent in excess of the truth when the arsenic content is about 0.05 per cent. Cast iron and ingot iron frequently contain this amount of arsenic so that it would seem advisable to take the effect of arsenic into consideration. To make sure that the precipitate of ammonium phosphomolybdate contains none of the corresponding arsenic compound the best way is to remove the arsenic from the solution. Various methods of accomplishing this have been proposed but the hydrobromic acid method to be described accomplishes this most simply and the use of the method is recommended in all cases

[1] The residue is not pure sodium titanate as this is hydrolyzed to form an insoluble acid titanate, *i.e.*, a compound containing a high TiO_2 content.

[2] *Stahl u. Eisen*, **28**, 295. See also CAMPBELL, *J. Anal. and Appl. Chem.*, **1893**, 2.

where an accurate determination of phosphorus is desired in the possible presence of arsenic.

Principle.—If a solution containing arsenic acid, phosphoric acid and ferric chloride is treated with pure hydrobromic acid (d. 1.42) and evaporated on the steam bath, then, as Rothe showed, all of the arsenic acid is volatilized, probably as arsenic tribromide, and there is no loss of phosphoric acid. Since ferric bromide does not interfere with the precipitation of ammonium phosphomolybdate it is evident that the determination of the phosphorus can be made in the solution freed from arsenic by any of the methods already described.

Commercial hydrobromic acid almost always contains a little phosphoric acid as impurity. If there is only little of it present, the simplest way is to carry out a blank phosphorus determination using the same quantities of reagents as in the analysis proper, and make a deduction from the results obtained in the analysis. If, however, there is much phosphoric acid present in the hydrobromic acid, it must be purified by distilling it.

Procedure.—Dissolve 5 g. of the iron or steel in nitric acid (d. 1.2), and treat the solution exactly as described on p. 96. To the hydrochloric acid filtrate from the silica precipitate, or to an aliquot part of it when considerable phosphorus is present, add 10 to 20 c.c. of pure hydrobromic acid (d. 1.42 containing about 48 per cent HBr by weight) and evaporate to dryness on the steam bath.

The hydrobromic acid should not be added to a very concentrated solution of ferric chloride on account of the danger of loss by spattering.

The residue obtained after evaporation is dark red; dissolve it in a little hydrochloric acid and rinse the solution into a beaker of 150 to 250 c.c. capacity. Remove the excess of free acid by evaporation and continue the analysis as on p. 97 weighing the phosphorus as ammonium phosphomolybdate.

9. DETERMINATION OF PHOSPHORUS IN MATERIALS CONTAINING TUNGSTEN

Principle.—Hinrichsen[1] has shown that when tungsten is present and the determination of phosphorus is carried out by the

[1] *Mitt. kgl. Materialprüfungsamt*, **28**, 229 (1910).

above method, the ammonium phosphomolybdate precipitate contains tungsten. He finds that if the precipitate is dissolved in ammonia and the ammoniacal solution treated with magnesia mixture while hot, according to the method of Jörgensen,[1] that the resulting precipitate does not contain tungsten. If the precipitation takes place in the cold, however, tungsten is present in the magnesium ammonium phosphate.

Solutions Required.—*Magnesia Mixture.*—Jörgensen recommends that the solution be prepared from 50 g. of crystallized magnesium chloride ($MgCl_2 \cdot 6H_2O$) and 150 g. of ammonium chloride per liter.

Acid Ammonium Nitrate Solution.—Dissolve 150 g. of ammonium nitrate in water, add 10 cc. of concentrated nitric acid and dilute to 1 liter.

Procedure.—Dissolve 5 g. of the sample in nitric acid (d. 1.20), evaporate the solution to dryness, and decompose the nitrates by ignition. Cool, moisten with concentrated hydrochloric acid, and warm with the addition of more hydrochloric acid until the iron is all in solution. Evaporate to dryness again and render the silica and tungsten insoluble by heating to 135° until no more vapors of hydrochloric acid are evolved. Cool, dissolve in as little strong hydrochloric acid as possible and evaporate off as much of the excess acid as can be accomplished without causing the deposition of solid ferric salt. Allow to stand some time and then add dilute hydrochloric acid and filter.

Wash the residue with dilute hydrochloric acid until the iron is nearly all removed and finish washing with the acid ammonium nitrate solution; this serves to prevent tungstic acid from forming a colloidal solution and passing through the filter.

Ignite the residue and volatilize the silica in it by treatment with sulfuric and hydrofluoric acids. Fuse with sodium carbonate, extract the melt with water and treat the hot solution with magnesia mixture as in the main solution. In this way the small amount of phosphoric acid is recovered that is deposited with the silica and tungstic acid.

The filtrate from the silica precipitate contains most of the phosphorus; it may also contain a little colloidal tungstic acid. Evaporate the solution (in a 150 or 250-c.c. beaker) as far as possible without separation of solid, and precipitate the phosphoric

[1] *Z. anal. Chem.*, **45**, 273 (1906).

acid by ammonium molybdate as described on p. 97. Filter and wash with acid ammonium nitrate solution.

Dissolve the precipitate in a very little 2.5 per cent ammonia, receiving the filtrate in a 150-c.c. beaker. Usually it is possible to keep the volume of solution down to 20 c.c. Cover the beaker with a watch-glass and heat until the solution begins to boil. Add neutral magnesia mixture, drop by drop, as long as any precipitate forms and 1 or 2 c.c. in excess. A flocculent precipitate first forms which soon becomes more compact and crystalline.

Stir the solution frequently as it cools and allow it to stand at least 4 hr. before filtering. Wash the precipitate with 2.5 per cent ammonia (1 vol. ammonia, d. 0.96, and 3 vol. water) and ignite it in a weighed crucible.

If there is only a small precipitate of magnesium ammonium phosphate it is better to dissolve it in nitric acid (d. 1.2) and precipitate again with molybdate solution, adding enough solid ammonium nitrate so that the solution contains 25 per cent of it. Weigh this precipitate as described on p. 97.

10. DETERMINATION OF PHOSPHORUS IN MATERIALS CONTAINING VANADIUM

(*Vanadium Steel and Ferro-vanadium*)

Principle.—In precipitating phosphoric acid in the presence of vanadic acid, the ammonium phosphomolybdate precipitate is not a pure yellow but has an orange-red shade owing to presence of vanadium. It is not possible to remove the vanadium by the method which is applicable when tungsten is present for the vanadium follows the phosphorus in every precipitation. On the other hand, the vanadium may be precipitated quantitatively from the ammoniacal solution of the yellow precipitate by the addition of ammonium chloride. The phosphorus and molybdenum remain in solution.

After the removal of the ammonium vanadate, the phosphoric acid may be determined in the usual manner.

Procedure.—Dissolve from 5 to 10 g. of the sample in nitric acid (d. 1.2) and remove the silicon as described on p. 96. In the filtrate from the silica, precipitate the phosphorus according

to p. 97 and filter off the orange tinted precipitate. Wash thoroughly with acid ammonium nitrate solution, dissolve the precipitate in ammonia, receiving the solution in a 150-c.c. beaker, and concentrate the solution to about 20 c.c.

During the evaporation of the solution, add a drop of ammonia from time to time; if the solution turns yellow the ammonia should make it colorless again.[1] To the cold, slightly ammoniacal solution add 5 or 6 g. of solid ammonium chloride and stir vigorously so that the solution quickly becomes saturated with the salt. If the quantity of vanadium present is not too small, the solution will become turbid as the ammonium chloride dissolves and a fine, flocculent precipitate of ammonium metavanadate will separate out; the precipitation is complete after about 6 hr.

Filter off the precipitate and wash it with a saturated solution of ammonium chloride (250 g. to the liter) until a little of the filtrate gives no test for molybdenum.

Slightly acidify the filtrate with dilute nitric acid and add a little more ammonium molybdate. Owing to the large amount of ammonium chloride present, the ammonium phosphomolybdate is now precipitated with an excess of molybdic acid in a finely pulverulent form. Dissolve the precipitate in 2.5 per cent ammonia and precipitate the phosphorus as magnesium ammonium phosphate as described on p. 97, weighing it as magnesium pyrophosphate.

[1] If, besides the vanadium, tungsten is also present, it must be removed with the silica, according to p. 112. Otherwise some of the tungstic acid will remain in the solution and cause difficulty. The present of tungsten trioxide in the phosphomolybdate precipitate is shown by the fact that the ammoniacal solution of the precipitate is not colorless but yellowish green. From such a solution the vanadium cannot be precipitated satisfactorily by means of ammonium chloride.

CHAPTER V

SILICON

DETERMINATION IN MATERIALS SOLUBLE IN ACID

1. Solution of the Sample in Hydrochloric Acid

Principle.—On treating iron and steel with acid, the silicon present as silicide is changed to hydrated silicon dioxide, commonly called silica. It is possible that during the treatment with acid there is an intermediate formation of volatile, easily decomposable substances such as SiH_4 and $SiCl_4$. Thus when iron silicide reacts with hydrochloric acid, the reaction

$$FeSi + 6HCl = FeCl_2 + SiCl_4 + 3H_2$$

may take place, but the silicon chloride, as fast as it is formed, reacts with the water present to form hydrated silicon dioxide:

$$SiCl_4 + 2H_2O = SiO_2 + 4HCl$$

This second stage of the reaction takes place so quickly that there is never any loss of silicon by volatilization (*cf.* Test Analyses, p. 122). The silicon dioxide, to a considerable extent, remains dissolved as colloid (*sol*). By evaporating the hydrochloric (or sulfuric) acid solution and heating the residue to at least 135° the colloidal silicic acid becomes dehydrated sufficiently to convert the colloid into the insoluble form (*gel*) and by washing with hydrochloric acid it can be freed from the soluble chlorides of the other metals.

Procedure.—Weigh out 2 to 4 g. of gray cast iron or silicon steel (up to 5 per cent Si), or 5 to 10 g. of white cast iron, ingot iron, wrought iron or ordinary steel, into a porcelain casserole of 12 to 15 cm. diameter. Cover the casserole with a watch-glass and dissolve the metal in hydrochloric acid, d. 1.12, using 10 c.c. of acid for each gram of metal.

When the main reaction is over, place the casserole on the water bath and heat till the solution of the material is complete. Then rinse off the bottom of the watch-glass, to remove any silicon dioxide that may have spattered upon it, and

evaporate to dryness. Place the dish containing the dry residue upon a Finkener tower (Fig. 19) and heat for about an hour, until no more fumes of hydrochloric acid are evolved and the contents of the dish have become brown. During this heating, the dish should be frequently turned to secure uniform heating of the residue. Instead of using the Finkener tower, the casserole and its contents may be heated for an hour in a hot closet kept at about 135° or upon a sand bath.

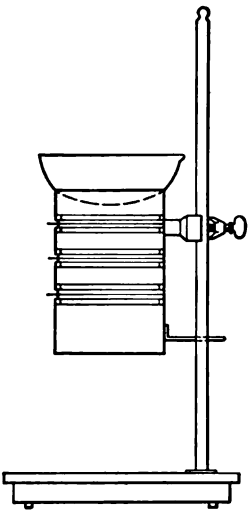

FIG. 19.

After the above heating, cover the dish with a watch-glass and allow it to cool. Without removing the watch-glass, cover the cool residue with hydrochloric acid (d. 1.12), using about 10 c.c. for each gram of original substance, and heat upon the water bath until the chlorides are entirely dissolved, from time to time stirring the liquid with a glass rod.

If a dark-brown residue of ferric oxide or basic salt remains undissolved at the bottom of the dish, it is because the residue was heated too strongly. In such cases, evaporate the solution again to dryness and, without further heating, take up the residue in concentrated hydrochloric acid (d. 1.2).

Dilute the solution with about 150 c.c. of water, heat nearly to boiling, and filter promptly[1] through a 9-cm. filter.[2]

If the original material contained considerable silicon and there is danger of the filter becoming clogged or of the filtrate running through turbid, it is well to add some filter-paper pulp before filtering. The pulp is prepared by shaking small pieces of filter paper with hot water in a stoppered Erlenmeyer flask.[3]

[1] If the solution stands long before filtering a little silica dissolves.

[2] In all cases where the precipitate is to be weighed, a filter washed with sulfuric and hydrofluoric acids must be used; the ash of such a filter weighs less than 0.1 mg.

[3] The rate at which the solution runs through the filter is influenced largely by the way the paper is folded (*cf.* RAASCHOU, *Z. anal. Chem.*, **49**, 759 (1910). Filters which lie against the funnel all along the sides often work badly,

After all the liquid has passed through the filter, transfer as much as possible of the precipitate to the filter by means of a stream of water from the wash bottle, and remove the last traces of precipitate from the sides of the dish by rubbing with a piece of filter paper which has been moistened with alcohol. The paper may be rubbed directly with the finger or with the aid of a glass rod covered on the end with smooth rubber tubing (a "policeman").[1]

Wash the filter and residue with hot, dilute hydrochloric acid (1 : 5) until the filtrate gives no blue color with potassium ferricyanide solution. While still moist, place the filter and precipitate in a weighed platinum crucible, place the latter on its side in a triangle and dry carefully by a small flame placed near the mouth of the crucible. When all the moisture has been expelled, transfer the flame to the base of the crucible and destroy the paper at as low temperature as possible without allowing it to take fire. Finally ignite strongly, using the blast lamp if

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whereas filters which adhere to the sides of the funnel only near the top, with the rest of the paper hanging free, permit the more rapid passage of the solution through them. For this reason, it is well to make the second fold of the filter a little wider than a right angle. To prevent the formation of a channel through which a part of the precipitate may be sucked, it is well to tear off a little of the inside edge as shown in Fig. 20.

FIG. 20.

To place the paper in the funnel, take hold of the funnel with the left hand, insert the folded filter and hold it firmly in position with the index finger of the left hand. Then fill the filter with water by a stream from the wash bottle, stopper the funnel tube with the finger, raise the filter a little to allow the air in the funnel tube to escape, replace the filter in its proper position and press out the air bubbles between the paper and the glass sides of the funnel. Then allow the water to run through the funnel and pour more water upon the filter.

In filtering, keep liquid in the funnel but do not allow the level to rise higher than the top of the paper.

Under no circumstances should a filter be used that is large enough to completely fill the funnel. The use of a filter extending above the funnel is never permissible in quantitative work.

[1] When a little tungsten is present, a yellow film usually adheres very firmly to the sides of the procelain dish. This may be removed by rubbing with filter paper moistened with ammonia. (*cf.* Tungsten, p. 199.)

the quantity of silica is considerable. Cool in a desiccator[1] and weigh. Repeat the ignition and weighing until a constant weight is obtained.

In the analysis of white cast iron, wrought iron, steel, etc., the precipitate of silicon dioxide usually appears gray colored on the filter but is perfectly white after being ignited. In no case, however, where accurate results are desired, should it be regarded as perfectly pure but its purity must be determined by treatment with sulfuric and hydrofluoric acids, whereby volatile silicon fluoride is formed.

To this end, moisten the silicon dioxide in the platinum crucible with sulfuric acid[2] (1 : 1), add from 1 to 3 c.c. of pure hydrofluoric acid,[3] and evaporate as far as possible on the water bath. Place the crucible on the Finkener tower[4] and gradually raise the temperature until all the free sulfuric acid has been expelled, then decompose any sulfates by direct ignition over the free flame, using a high temperature at the last, cool in a desiccator, and weigh. The loss on volatilization represents the weight of pure SiO_2:

$$SiO_2 + 4HF = SiF_4 + H_2O$$

[1] *cf.* p. 82, footnote.

[2] The addition of the sulfuric acid has a double purpose. On the one hand, it aids the reaction between silica and hydrofluoric acid by acting as a dehydrating agent and prevents the formation of fluosilicic acid by the interaction of silicon fluoride and water. On the other hand, it prevents the volatilization of other fluorides, such as those of aluminium, iron, chromium, titanium and vanadium. When these last-mentioned elements are present, they will be volatilized to some extent as fluorides, if too little sulfuric acid is used, and the silicon result will be too high. Sulfuric acid decomposes these fluorides before their boiling points are reached and the sulfates are decomposed upon further heating into oxide and volatile sulfuric anhydride, thus leaving them in the same condition as before the treatment. The amount of sulfuric acid to be added should be regulated by the probable amounts of these impurities. When tungstic acid is present, the ignition before and after treatment with hydrofluoric acid must *not* be over the blast lamp. Tungstic acid is slightly volatile when heated with sulfuric acid in a platinum crucible.

[3] The purity of the acid should be tested by evaporating some of it to dryness and making sure that there is no weighable residue after ignition.

[4] Instead of using the water bath and Finkener tower, the evaporation of the acid may take place by suspending the crucible in a larger iron crucible (by inserting platinum wires in the latter) and heating over the free flame.

Usually, in spite of all the pains that may be taken with the analysis, small quantities of ferric and manganic oxides remain behind after the treatment with hydrofluoric acid, and in the analysis of steels containing tungsten, titanium, chromium, and vanadium these elements are invariably present in the residue to a greater or less extent.

In the determination of silicon in gray cast iron, all the graphite remains behind with the silica and care should be taken to burn it completely before weighing. It is almost impossible to obtain a silica precipitate so pure that the treatment with hydrofluoric acid is unnecessary but a more complete removal of the iron may be accomplished if, after washing with dilute hydrochloric acid on the filter, the silica is washed well with alcohol to remove substances formed by the decomposition of carbide, and again with hydrochloric acid to the disappearance of the iron test.

Small quantities of silicic acid remain in the first filtrate but when the work is done carefully according to the above directions the silica thus lost will rarely amount to more than a fraction of a milligram and this is more than balanced by the amount of silica that is obtained from the reagents and from the dishes. In iron and steel analysis, therefore, it is unnecessary to evaporate the filtrate from the silica precipitate to recover more silica, although this is usually necessary in the analysis of silicates.

The filtrate from the silica determination, together with any residue from the treatment with hydrofluoric acid, may be used for the determination of manganese, copper, nickel, chromium, aluminium, etc., but not for the determination of phosphorus or sulfur.

2. MODIFIED DROWN METHOD

In this method, which was proposed by T. M. Drown[1] and is regarded as a standard method in the United States, the sample is dissolved in a mixture of nitric and sulfuric acids and the solution is evaporated until copious fumes of sulfuric anhydride are evolved. The hot, concentrated sulfuric acid acts as an efficient dehydrating agent thus making the silicic acid insoluble.

[1] *J. Inst. Min. Eng.*, **7**, 346; *Am. Soc. Testing Materials*, **1915**, 217, 522.

Solutions Required.—*Nitro-sulfuric Acid.*—Mix 1,000 c.c. of concentrated sulfuric acid, d. 1.84, 1,500 c.c. of concentrated nitric acid, d. 1.42 and 5,500 c.c. of water.

Dilute Hydrochloric Acid.—Mix 100 c.c. of concentrated hydrochloric acid, d. 1.2, and 900 c.c. of distilled water.

Procedure.—Weigh 4.69 g. of steel into a 300-c.c. porcelain casserole, cover the dish with a watch-glass and dissolve the sample in 80 c.c. of the nitro-sulfuric acid. Heat until the steel is all dissolved, then remove the cover glass and evaporate slowly until copious fumes of sulfuric acid are evolved. During this evaporation the dish should not be covered even with a raised watch-glass because if water condenses on the watch-glass and drops down into the hot sulfuric acid it will cause spattering. Cool, add 125 c.c. of distilled water and heat with frequent stirring until all the salts are dissolved. Then add 5 c.c. of concentrated hydrochloric acid, heat 2 min. and filter on a 9-cm. filter. Wash the precipitate with hot, dilute hydrochloric acid till free from iron and then with hot water until free from acid. Ignite the precipitate and filter in a weighed platinum crucible and correct for impurities obtained after hydrofluoric acid treatment exactly as described in Method 1.

A blank determination should be made by carrying out the entire process exactly as described but with no steel in the casserole. The weight obtained in this blank determination should be deducted from the weight obtained in the analysis. The filtration and weighing of the filter must be carried out in this blank determination whether there is any visible precipitate or not. The silica obtained in the blank determination comes in part from the action of the acids on the porcelain dish but some always come from the action of the acids on the glass bottles in which they are kept.

By using the ten-fold factor weight, 4.69 g., the percentage of silicon is obtained by taking the weight of silicon dioxide in grams and moving the decimal point one place to the right.

Procedure for Cast Irons.—Use 1.17 g. of sample and 35 c.c. of the nitro-sulfuric acid. Otherwise, proceed exactly as in the analysis of steel. In this case, multiply the weight of silica in grams by 40 to get the per cent of silicon.

The American Society for Testing Materials also suggests a method for the analysis of steels which is practically the same except that the steel is dissolved directly in 15 c.c. of concentrated sulfuric acid and four times as much water, using a sample weighing 2.35 g.

3. NITRIC ACID METHOD

Weigh out the same amount of metal as stated for Method 1 and add 12 c.c. of nitric acid (d. 1.18) for each gram of metal. Add the acid in small portions, waiting each time till the violent reaction is over. When all the acid has been added, heat on a water bath until the sample has all dissolved. If there is turbidity due to a brown deposit, bring this into solution by adding more nitric acid and heating until eventually a fairly clear, more or less dark brown colored solution is obtained. Remove the watch-glass and evaporate on the water bath as near to dryness as possible. Since a film forms on the surface of the liquid which makes it difficult to evaporate to dryness, rotate the solution about the dish from time to time so that liquid collects on top of the dry layer.

It is not advisable to hasten the evaporation by constantly stirring with a glass rod because, during the subsequent heating, pieces of the glass are likely to splinter off from the rod and render the determination of the silicon inaccurate.

To remove all the nitric acid, heat the dish upon the Finkener tower or on a sand bath. Another way is to heat the dish on a piece of asbestos plate, 3 mm. thick, over a Fletcher burner, taking care to heat gently at first.

Care must be taken to avoid loss by spattering. When no more bubbles of gas are evolved, remove the cover glass and heat the contents of the dish still hotter until the nitrates are decomposed (in using the Finkener tower, remove the wire gauze). Finally, cover the dish with a watch-glass and ignite over a free flame until no more red vapors are evolved, showing that the decomposition of the nitrates is complete. The oxides are now dark brown and do not adhere very firmly to the sides of the casserole.

Allow to cool, moisten with a little concentrated hydrochloric

acid (d. 1.19) and warm for a short time. Then add 10 c.c. of hydrochloric acid (d. 1.12) for each gram of metal and heat, while stirring with a glass rod, until all the ferric oxide dissolves.

To make sure that the silicon dioxide is all in the insoluble condition, evaporate the hydrochloric acid solution to dryness and heat for some time at 135°. After cooling, moisten the residue with concentrated hydrochloric acid (d. 1.19) and then add the same volume of hydrochloric acid (d. 1.12) as before, dilute, filter and wash with dilute hydrochloric acid until the washings give no test for iron with potassium thiocyanate solution.

With material free from graphite, the silicon dioxide is obtained by this method in the form of a white or nearly colorless gelatinous precipitate; if tungsten is present it is indicated by its yellow color.

With materials containing graphite, the precipitate requires the same treatment as is recommended under Method 1. In all cases the treatment with hydrofluoric acid is necessary.

The filtrate from the silica can be used for the determination of substances such as manganese, copper, nickel, aluminium, chromium, phosphorus and iron, but not for the determination of sulfur.

Computation.—If p = wt. of SiO_2, s = wt. of substance, then

$$\text{Per cent Si} = \frac{\text{Si} \times p \times 100}{\text{SiO}_2 \times s} = \frac{46.93p}{s}$$

The computation is the same for all three of the methods.

Test Analyses.—Experiments with steel containing 0.33 per cent Si, silicon steel with 1.65 per cent Si, chrome steel with 0.20 per cent Si and chrome-tungsten steel with 0.23 per cent Si have shown that practically identical values are obtained with Methods 1 and 3 and the results by various chemists on standard steels and cast irons prepared by the Bureau of Standards at Washington, D. C., show that Method 2 is capable of giving equally exact results. A high-vanadium content of the steel does no harm.

Accuracy of the Results.—The chief sources of error in the determination of silicon are:

1. Silicic acid present in the acids.
2. Solution of silica from the porcelain dish.
3. Solubility of silicon dioxide in hydrochloric acid solutions containing ferric chloride.
4. Presence of non-volatile material (oxides of iron, aluminium or of the alkalies) in the hydrofluoric acid.

The first two sources of error tend to cause the results to come out too high and the last two sources tend to give too low results. The errors, therefore, may compensate one another.

The extent of error arising from the first and second sources should be determined by blank tests carried out with the same amount of acid as in the analysis. The quantity of silica thus found should be deducted from that obtained in the analysis. The silicic acid content of acids increases slowly up to a certain point upon standing in glass bottles. The silica obtained by evaporation in porcelain dishes is usually a very small quantity.

The hydrofluoric acid should be tested to see if the quantity used in the analysis leaves a weighable residue. This is not usually the case with the best grades of hydrofluoric acid.

As regards the solubility of silicon dioxide in hydrochloric acid solutions containing iron, there are very few statements in the literature. It is pretty certain, however, that this error is not large and probably does not exceed the error in weighing. There is always a tendency for the deposited gelatinous silicic acid to pass into the colloidal condition and this tendency becomes noticeable if the solution is allowed to stand some time before filtering.

It is probably safe to assume, however, that the error in a silicon determination when carefully carried out is not greater than ± 1 mg. and on a 1-g. sample this would amount to 0.05 per cent or on a 10-g. sample to 0.005 per cent. It follows, therefore, that the results should not be regarded as accurate beyond the second decimal and a silicon content below 0.01 per cent cannot be determined with accuracy by any one of the above methods.

Permissible Deviation of Silicon Values.—Corresponding to the sources of error and the accuracy attainable in the determination, the following table represents the allowable deviation in duplicate results on the same sample.

Si Content	Allowable Error
0.01 to 0.25 per cent	0.005 per cent
0.25 to 1.00 per cent	0.01 per cent
1.00 to 5.00 per cent	0.02 per cent
5.00 to 10.00 per cent	0.03 per cent

Applicability of Methods 1, 2, and 3.—All grades of iron and steel that are soluble in hydrochloric acid or nitric acid and most other metals or alloys that are soluble in these acids (*e.g.*, nickel, chromium, manganese, aluminium, zinc, molybdenum) may be analyzed for silicon by any of the above methods.

Irons containing up to 5 per cent silicon can be dissolved without much difficulty but incomplete solution always results when the silicon content is much higher; in such cases, therefore, these methods have no advantages over the fusion method described under **4.**

4. DETERMINATION OF SILICON IN MATERIALS INSOLUBLE IN ACID

Principle.—Finely pulverized metals and alloys can be attacked by heating with a mixture of pure sodium carbonate and pure magnesium oxide.

The chemical reaction that takes place is,[1] in the first place, an oxidation, and depends upon the tendency of sodium carbonate to decompose into sodium oxide and carbon dioxide; the latter acts upon the metals forming metal oxide and carbon monoxide.[2] Similarly, the reaction that takes place with the metalloid silicon may be expressed as follows:

$$(a)\ Na_2CO_3 \rightleftarrows Na_2O + CO_2$$
$$(b)\ Si + 2CO_2 = SiO_2 + 2CO$$
$$(c)\ SiO_2 + Na_2O = Na_2SiO_3$$

The addition of magnesium oxide prevents the mass from fusing and as a result the carbon monoxide passes off more readily and without the danger of loss by spattering that would result if the flux were liquid.

[1] Sodium carbonate alone may be used in some cases but the metal is attacked less readily and there is more danger of loss by spattering.

[2] Deiss, *Chem.-Ztg.*, **34**, 781 (1910).

After ignition, the mass is dissolved in water and dilute acid and the silica is determined as already described.

Ignition Mixtures.—It is well to have two mixtures at hand, one consisting of two parts sodium carbonate to one part magnesium oxide, the other of one part sodium carbonate and two parts magnesium oxide. The mixtures should be thoroughly incorporated by rubbing in a mortar. The first mixture was proposed by Rothe[1] and the second by Eschka.[2] As a rule the Rothe mixture is used but, when fusion results with it, the Eschka mixture is required.

Procedure.—The chief requirement for the success of the ignition process is that the material shall be in the form of very fine powder. The finer the powder, the more rapid and the more complete the attack. Coarse pieces may be broken up in a diamond mortar and then, if possible, ground in an agate mortar until all the powder passes through a 120-mesh sieve.

Of material rich in silicon (metallic silicon, ferro-silicon) take from 0.3 to 1 g., but of alloys with low silicon content (ferro-chrome, ferro-tungsten, etc.) take up to 5 g. For the ignition, a spacious platinum crucible is required and it should be thoroughly cleaned by fusing sodium carbonate in it and washing with water and dilute acid. Before introducing the sample, cover the bottom of the clean crucible with a layer 3 to 4 mm. deep of the sodium carbonate and magnesia mixture. Mix the weighed sample in a clean agate mortar with seven to eight times as much of the ignition mixture and then carefully transfer the powder to the crucible (using glazed paper beneath the crucible to catch any powder that is spilt). Clean the mortar and pestle by rubbing with a little more of the ignition mixture, and add the latter to the contents of the crucible. Then place the cover on the crucible and heat strongly for half an hour using a good burner, and finally heat ½ to 1 hr. over the blast lamp. Or, if an electric muffle furnace is at hand, it may be used to advantage. In this case the crucible should not come into direct contact with the glowing walls of the muffle as there is danger of both crucible and muffle being injured; the crucible should be placed upon a platinum triangle, with the three ends of the latter

[1] *Mitt. kgl. Materialprüfungsamt*, **25**, 51 (1907).

[2] *Z. anal. chem.*, **13**, 344 (1874).

bent vertically downward and resting on the bottom of the muffle (*cf.* Fig. 23, p. 177).

When the ignition is accomplished, remove the crucible and allow it to cool. The cake within the crucible should be sintered into a coherent mass without being at any place fused to the sides of the crucible. By simply inverting the crucible the cake should fall out, leaving the crucible nearly clean. The crucible is not attacked appreciably and experiments have shown that after igniting several grams of different alloys there is no sensible loss in weight of the crucible.

Soften the mass in a porcelain casserole by treatment with water; wash out the crucible well and dissolve any adhering solid by heating with dilute hydrochloric acid, adding the solution to the contents of the porcelain dish. Cover the dish with a watch-glass, add hydrochloric acid until the sodium carbonate is all decomposed and heat on the water bath until all the magnesia, iron oxide, etc., is dissolved. For 10 g. of the ignition mixture, about 45 c.c. of hydrochloric acid (d. 1.12) are required. Evaporate the solution on the bath as far as possible and complete the necessary dehydration of the silicic acid by the customary heating to 135°.[1] After cooling, moisten with concentrated hydrochloric acid (d. 1.19), add the usual quantity of hydrochloric acid (d. 1.12) and heat until all the soluble salts have dissolved.

Dilute the solution with water, filter off the silica, wash with dilute hydrochloric acid and test the filtrate for silica by evaporating again to dryness, repeating the treatment of the residue as above, and filtering through a fresh filter.

If the precipitated silicon dioxide should be contaminated with heavy dark particles of unattacked material (distinguishable from any graphitic particles by the gritty feeling under a stirring-rod) then the precipitate, after being washed well, must be ignited and fused with sodium carbonate in a platinum crucible. From this fusion, the silica is recovered in the same man-

[1] On account of the presence of magnesium chloride, the evaporation to dryness requires more time than usual and in the subsequent heating of the moist residue special care must be taken to avoid loss by spattering. The residue must not be heated above 135° as the magnesium chloride forms a basic salt which combines to some extent with silica if heated too much.

ner as described above for the treatment of the mass after the original ignition.

After igniting the silica to constant weight, determine its purity by treatment with sulfuric and hydrofluoric acids.

Applicability of the Ignition Method.—The method is suitable for the determination of silicon in metals and alloys which are insoluble or difficultly soluble in acids, provided it is possible to get them in finely powdered form. The method has to be modified for the analysis of titanium alloys, inasmuch as solutions containing titanium are likely to yield silica precipitates containing a large part of the titanium in the form of hydrated titanium dioxide.

Modification of the Silicon Determination for Titanium Alloys.—Decompose the titanium-silicon alloy with the Rothe or Eschka mixture in the usual manner and soften the ignited mass with cold water; triturate the sintered lumps in an agate mortar and rinse everything into a beaker. Carefully avoiding any heating of the solution, add hydrochloric acid (d. 1.12) until the liquid is strongly acid. Allow the contents of the beaker to stand for an hour or two in the cold. Then heat slowly on the water bath, with frequent stirring, until a clear solution is obtained in the course of a few hours. Add 20 c.c. of sulfuric acid (1 : 1) and evaporate until all the hydrochloric acid is expelled. Transfer the contents of the beaker to a platinum dish and heat on the Finkener tower until white fumes of sulfuric anhydride are evolved. As soon as this is accomplished, stop heating and allow the dish to cool. Add water to the residue, filter off the silica and wash it free from iron with dilute hydrochloric acid. Ignite, weigh and treat with sulfuric and hydrofluoric acids as usual.

Test Analyses.—In the analysis of metallic titanium, duplicate determinations on 1-g. samples gave 4.79 per cent and 4.69 per cent Si. In the analysis of ferro-titanium, 0.85 and 0.51 g. of material were taken for analysis and the results obtained were 3.65 per cent and 3.60 per cent Si.

CHAPTER VI

SULFUR

Sulfur, to some extent, occurs in all kinds of iron and steel but the maximum quantity ever found is only a few tenths of 1 per cent. It is always present in the form of sulfides, chiefly of iron and manganese, and such sulfur can be evolved as hydrogen sulfide by treatment with hydrochloric acid. Since sulfur tends toward segregation, care should be taken to procure a good average sample and to use a fairly large amount of material for the analysis.

The gravimetric methods usually depend upon the oxidation of the sulfur to the sulfate condition and its precipitation as barium sulfate. Morrell,[1] however, weighs the sulfur as cadmium sulfide and Berzelius obtained a precipitate of silver sulfide, dissolved it in nitric acid and weighed the silver as chloride. The problem of determining sulfur in the presence of iron has received a great deal of attention in the literature. Küster and Thiel[2] have shown that enormous errors, sometimes amounting to a loss of one-tenth the entire sulfur content, result from the addition of barium chloride to a boiling solution containing sulfuric acid in the presence of ferric chloride. The loss is due probably in part to the formation of a complex ion containing iron and sulfur which is not completely precipitated and partly to the fact that ferric sulfate, or any complex containing iron and sulfur, loses sulfur upon ignition. These low results, therefore, occur especially when the precipitate is strongly contaminated with iron, as shown by the red stain of ferric oxide in the crucible after the final ignition. Küster and Thiel found that accurate results could be obtained without the removal of the iron in three ways: (1) by precipitating with ammonia without filtering, heating nearly to boiling, adding the barium chloride slowly, and finally dissolving the ferric hydroxide in dilute hydrochloric acid; (2) by precipitating with barium chloride in a cold solution; (3) by adding the cold ferric

[1] *Chem. News*, **28**, 229.

[2] *Z. anorg. Chem.*, **22**, 424.

chloride and sulfuric acid solution very slowly to a boiling, dilute solution of barium chloride. It is well to remember, however, that the trouble caused by the ferric chloride in the determination of small quantities of sulfur is probably greater in dilute than in concentrated solutions, as Archbutt[1] has shown. On the other hand, barium sulfate has a decided tendency to occlude impurities, and occlusion is likely to be greater in concentrated solutions. In determining large quantities of sulfur, therefore, it is best to work in dilute solutions.

To avoid the harmful effect of ferric chloride upon the sulfur determinations, it has been recommended to reduce the iron to the ferrous condition but this remedy is not usually adopted in iron and steel analysis. A more common expedient is to determine the sulfur in a solution free from iron. This may be accomplished: (1) by expelling the sulfur as hydrogen sulfide and oxidizing the absorbed gas; (2) by removing the ferric chloride by shaking the solution with ether; (3) by precipitating the iron with an excess of ammonia or of sodium carbonate; (4) by treating the iron or steel with acid cupric ammonium chloride, which dissolves the iron and leaves the sulfur in the residue from which it can be obtained by an oxidizing solution and treatment with barium chloride.[2]

The volumetric determination of sulfur in iron and steel is usually based upon the expulsion of the sulfur as hydrogen sulfide and the reaction of this gas with iodine. The details of the method vary considerably, especially with regard to the preliminary absorption of the hydrogen sulfide.

The best-known colorimetric method is that of J. Wiborgh[3] which depends upon the evolution of the sulfur as hydrogen sulfide, the passage of the gas through a cloth disk which has been dipped in cadmium acetate solution, and the subsequent comparison with a series of similar disks produced by the treatment of steels with known sulfur content. This method is useful in a busy laboratory.[4]

[1] *J. Soc. Chem. Ind.*, **1890**, 25.

[2] MEINECKE, *Chem. News*, **59**, 107; BOUCHER, *ibid.*, **74**, 76; CARNOT and GOUTAL, *J. Chem. Soc.*, **72**, II, 520.

[3] *Stahl u. Eisen*, **6**, 240 (1866).

[4] *cf.* TREADWELL-HALL, "Analytical Chemistry," Vol. II.

1. DETERMINATION OF SULFUR IN THE PRESENCE OF IRON

In spite of the many objections that have been raised to the direct determination of sulfur in the presence of iron, many chemists still adhere to the old method of dissolving the sample in nitric acid or in aqua regia, evaporating to render the silica insoluble, and precipitating the sulfuric acid from a concentrated solution in the presence of ferric chloride. The method has been used by the Bureau of Standards, Washington, D. C. in the analysis of standardized specimens of iron and steel and the results have compared favorably with those obtained by other methods.

Treat 5.50 g. of borings with 45 c.c. of concentrated nitric acid and 5 c.c. of concentrated hydrochloric acid in a 400-c.c. beaker. Add 0.5 g. of sodium carbonate and evaporate to dryness. Bake to decompose nitrates, dissolve the residue in 30 c.c. of concentrated hydrochloric acid, and again evaporate to dryness for the purpose of making the silica insoluble. Redissolve the residue in 30 c.c. of strong hydrochloric acid, evaporate the solution to sirupy consistency, and add 4 c.c. of concentrated hydrochloric acid. When all the iron is in solution, add 30 to 40 c.c. of hot water, filter off the silicious residue and wash with hot water. Avoid letting the filtrate exceed 100 c.c. Heat it to boiling and precipitate with 10 c.c. of 10 per cent barium chloride solution. Allow to stand 24 hr. before filtering.

Fuse the insoluble silicious residue with sodium carbonate and a little potassium nitrate, extract the fusion with hot water, filter, acidify with hydrochloric acid, and evaporate to dryness. Moisten the residue with hydrochloric acid, dilute and filter. Heat to boiling, precipitate hot with 2 c.c. of barium chloride solution, and allow to stand over night. The sulfur obtained from this insoluble residue should be added to that obtained from the main solution.

Evaporations should take place in an atmosphere free from vapors containing sulfur and the use of steam baths, electrically heated hot plates, or alcohol burners is to be preferred to gas flames. A careful blank experiment should be carried along at the same time, using the same quantities of reagents and exactly the same operations.

The precipitate of barium sulfate obtained in the presence of the iron should be washed with a hot solution of 2 c.c. concentrated hydrochloric acid and 1 g. of barium chloride per liter until free from iron and then with hot water till free from chloride. The second precipitate may be washed with hot water alone.

Since the weight of sample recommended is four times the value of the chemical factor $\frac{S}{BaSO_4}$ it is evident that the percentage of sulfur in the sample is equal to one-fourth of the weight of the barium sulfate precipitate when expressed in centigrams.

The above method is suitable for the analysis of cast iron as well as steel and is recommended by the American Society for Testing Materials.

2. BAMBER METHOD FOR DETERMINING SULFUR IN IRON OR STEEL

This method is suitable for the analysis of cast iron or steel and for any iron alloys which are decomposed completely by treatment with nitric acid. It has proved to be a very reliable method.

Procedure.—Dissolve from 3 to 5 g. of the sample in concentrated nitric acid (d. 1.42). After the iron has dissolved completely, add 2 g. of solid potassium nitrate and evaporate to dryness on the water bath in a platinum dish. Heat the residue to redness using an alcohol flame. After the ignition, add 50 c.c. of a 1 per cent solution of sodium carbonate, boil for a few minutes and filter. Wash the precipitate thoroughly with hot 1 per cent sodium carbonate solution. Acidify the filtrate with hydrochloric acid and evaporate to dryness. Moisten the residue with 2 c.c. of concentrated hydrochloric acid and add 50 c.c. of water. Heat to boiling and filter. Dilute the filtrate to 100 c.c. and precipitate the filtrate with 10 c.c. of 2 per cent barium chloride solution. Ignite and weigh in the usual manner.

3. DETERMINATION OF SULFUR BY THE ETHER METHOD[1]

Necessary Apparatus and Solutions.—The requirements are the same as those specified on pp. 71, 72.

[1] *cf.* KRUG, *Stahl u. Eisen* **25**, 887 (1905).

Procedure.—Weigh 5 g. of borings into a 500-c.c. round-bottomed flask and add 50 c.c. of concentrated nitric acid (d. 1.42). As a rule there is little action in the cold. Heat cautiously at first, holding the flask with a clamp and rotating it over a small flame, and have a dish of cold water ready so that the flask may be placed in it if the reaction should become too violent. After the brown nitrous fumes cease to form, gradually raise the temperature of the acid until it boils. When, at the end of an hour or so, the sample is all dissolved, add 0.25 g. of potassium nitrate dissolved in a little water, evaporate to dryness and heat the residue until no more brown fumes are evolved. After cooling, dissolve the residue by heating it with 50 c.c. of concentrated hydrochloric acid (sp. gr. 1.2) and again evaporate to dryness. Redissolve in hydrochloric acid, dilute somewhat and filter off the silicious residue. Evaporate the filtrate until a film of ferric chloride forms and redissolve this film by a few drops of hydrochloric acid. It is now ready for treatment with ether.

After cooling the ferric chloride solution, introduce it into the double separatory funnel shown in Fig. 13, p. 71, and wash out the contents of the dish, or beaker, with hydrochloric acid (d. 1.1) keeping the total volume of the solution and washings below 60 c.c. Add 30 c.c. of the mixture of ether and concentrated hydrochloric acid (*cf.* p. 71) and 100 c.c. of pure ether. Cool under the water tap and shake thoroughly. The upper, olive-green, ether layer now contains nearly all the iron and the lower, aqueous layer contains all the sulfuric acid. Carefully transfer the lower layer to the other separatory funnel. Add to the ether solution remaining in the upper funnel, a few cubic centimeters of ether saturated with dilute hydrochloric acid (sp. gr. 1.1). Shake, allow to settle and add the lower layer to the solution in the lower funnel. Introduce 75 c.c. of pure ether into this funnel, shake well and finally draw off the lower layer into a porcelain evaporating dish; it contains all the sulfur, very little ferric chloride and some dissolved ether. Evaporate to dryness on the water bath, moisten the residue with a few drops of hydrochloric acid, dilute with a little water and filter into a small beaker. Heat the filtrate to boiling and precipitate the sulfuric acid in the usual way.

Allow the beaker to stand in a warm place for several hours,

then filter, wash, ignite and weigh as described under the previous method. It is important to carry out simultaneously with the analysis a blank experiment with the same quantities of reagents.

4. IODOMETRIC DETERMINATION OF SULFUR IN STEEL

The iodometric determination of sulfur in iron alloys is based upon the following reactions:

$$FeS + 2HCl = FeCl_2 + H_2S$$
$$H_2S + I_2 = 2HI + S$$

and, when an excess of iodine is used,

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

Usually the gas which escapes on dissolving the sample in hydrochloric acid is not allowed to act directly upon iodine but it is first absorbed by some suitable reagent. Sodium hydroxide or ammoniacal cadmium chloride solution is commonly used but many other absorbents have been proposed. With sodium hydroxide, the resulting solution, which contains the sulfur as sodium sulfide, is diluted to about 500 c.c. and acidified with hydrochloric acid. A little potassium iodide is added and the hydrogen sulfide is at once titrated with a standard iodine solution, using starch as an indicator. Two objections may be raised to this procedure. First, it is possible that some gas other than hydrogen sulfide may be absorbed by the sodium hydroxide solution and subsequently react with iodine. Second, there is opportunity for a little hydrogen sulfide to escape when the solution is acidified just before the titration.

When an ammoniacal solution of cadmium chloride is used as the absorbent, both of the above objections may be overcome. Cadmium sulfide is precipitated in the liquid absorbent, the precipitate is removed, treated with a measured volume of standard iodine solution, the solution acidified and the excess of iodine titrated slowly with sodium thiosulfate solution.

Apparatus and Solutions.—A simple and suitable evolution apparatus may be constructed as follows: Use a 250-c.c. round-bottomed flask as generator. Fit it with a double-perforated rubber stopper. Through one hole in the stopper introduce a dropping funnel so that the bottom of the stem reaches nearly to

the bottom of the flask and through the other hole introduce a delivery tube, bent twice at right angles, starting from just below the bottom of the rubber stopper in the round-bottomed flask, leading into a 250-c.c. Erlenmeyer flask, and reaching nearly to the bottom of this flask. Connect this flask with a second 250-c.c. Erlenmeyer flask by means of another tube bent twice at right angles. This tube starts just below the stopper in the first flask and extends nearly to the bottom of the second flask. Connect this flask with a third Erlenmeyer flask in the same way. The first Erlenmeyer serves merely as a guard flask and to remove most of the hydrochloric acid that distils over, whereas the second and third flasks are to contain liquid into which the gas is to be led.

Prepare a solution of sodium thiosulfate by dissolving 5 g. of the crystallized salt, $Na_2S_2O_3 \cdot 5H_2O$, in each liter of freshly boiled and cooled water. Prepare a solution of iodine by dissolving 2.5 g. of iodine in 100 c.c. of water containing 5 g. of pure potassium iodide, finally diluting the solution to 1 liter. Both of these solutions are approximately 0.02-normal. Titrate the two solutions against one another and then standardize the sodium thiosulfate against potassium permanganate, p. 62, against pure iodine, p. 156, or against copper, p. 147.

For absorbing the hydrogen sulfide, prepare an ammoniacal solution of cadmium salt by dissolving 120 g. of cadmium chloride in 1,500 c.c. of water and adding 600 c.c. of concentrated ammonia (d. 0.90). Use 10 c.c. of this solution in each of the two absorbing flasks, diluting with 50 c.c. of water. If a white precipitate of cadmium hydroxide appears upon dilution, dissolve it by the addition of a little ammonia. Place 25 c.c. of water in the first Erlenmeyer flask. This serves to catch most of the hydrochloric acid that distils over, but it does not absorb an appreciable amount of sulfur as it is heated nearly to boiling toward the last.

Procedure.—Weigh 5 g. of steel into the generating flask, make sure that all the connections are tight and then add 60 c.c. of strong hydrochloric acid (d. 1.19) through the funnel.[1] As soon as the action of the acid on the metal begins to slacken, gradually apply heat, and finally, when all the metal is dissolved,

[1] If dilute hydrochloric acid is used, lower results are obtained, *cf.* pp. 135, 138.

boil the solution gently until steam condenses in the guard flask. Disconnect the apparatus, first opening the stopper of the dropping funnel so that there will be no back pressure on the removal of the flame.

Filter off the precipitate of cadmium sulfide, which is usually all in the middle flask, and wash the flask and filter twice with water. Transfer the filter and precipitate to a beaker, pour over it 300 c.c. of water, add 25 c.c. of the standard iodine solution, stir thoroughly and then add 5 c.c. of concentrated hydrochloric acid. Dissolve any sulfide precipitate remaining in the flask, or in the glass tubing, by means of a little of this solution, washing it all back into the beaker. Titrate the excess of iodine with the standard sodium thiosulfate solution.

Computation.—If s represents the weight of the steel, n the cubic centimeters of thiosulfate used, T the value of 25 c.c. of iodine solution in terms of the thiosulfate solution, and N the relation of the thiosulfate to the normal solution, then

$$\text{Per cent } S = \frac{(T - n)\,N \times 1.6}{s}$$

5. DETERMINATION OF SULFUR BY THE SIMPLIFIED EVOLUTION METHOD

For the routine analysis of steel the American Society for Testing Materials recommends a method similar to that last described but with much simpler apparatus. The method is not recommended for the analysis of cast irons nor considered reliable for all kinds of steel, some of which contain a little sulfur which is not easily converted into hydrogen sulfide on treating the sample with hydrochloric acid.

T. G. Elliot, however, finds that annealing the sample with a little potassium ferrocyanide (yellow prussiate of potash) makes it possible to get all the sulfur into the desired condition. The annealing is accomplished by mixing a 5-g. sample of the metal with 0.25 g. of anhydrous ferrocyanide and heating in a covered porcelain crucible for 20 min. at 750 to 850° after which the sample is allowed to cool slowly and is broken up in a mortar.

The concentrations of the hydrochloric acid and ammoniacal cadmium chloride solution are different from those recommended

in Method 3 and instead of oxidizing the hydrogen sulfide with pure iodine solution, it is accomplished by means of potassium iodate and iodide. The reactions involved in the titration are as follows:

$$KIO_3 + KI + 6HCl = 6KCl + 3I_2 + 3H_2O$$
$$I_2 + H_2S \rightarrow 2HI + S$$

The iodine color is not permanent until all the H_2S is oxidized.

Solutions Required.—*Hydrochloric Acid Approximately 6-normal.*—Dilute hydrochloric acid, d. 1.2 with an equal volume of water.

Ammoniacal Cadmium Chloride.—Dissolve 10 g. of cadmium chloride in 400 c.c. of distilled water and add 600 c.c. of concentrated ammonium hydroxide (d. 0.90).

Potassium Iodate.—Dissolve 1.116 g. of potassium iodate (weighed accurately) and 12 g. of potassium iodide (weighed roughly) in 1,000 c.c. of water. One cubic centimeter of the solution = 0.0005 g. sulfur or 0.01 per cent when a 5-g. sample of steel is used. The sulfur value should be checked by analyzing a steel of known sulfur content by the method. Bureau of Standards Standard Steel No. 8a is recommended for this purpose.

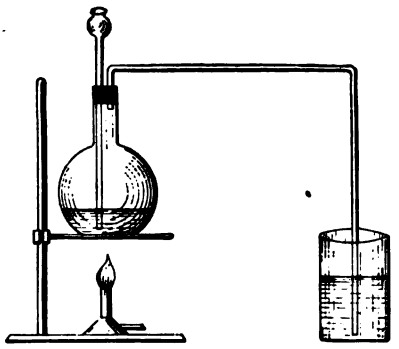


FIG. 21.

Starch.—Triturate 6 g. of soluble starch with cold water, into a thin paste and rinse this into 1,000 c.c. of boiling water. Add a solution of 6 g. zinc chloride in 50 c.c. of water and mix well: with this addition the starch solution keeps better than in pure water.

Procedure.—Weigh 5 g. of steel into the 500-c.c. flask shown in Fig. 21. Make the connections as shown in the drawing and place 10 c.c. of ammoniacal cadmium chloride solution mixed with 150 c.c. of distilled water in the glass tumbler. Add 80 c.c. of 6-normal hydrochloric acid through the thistle tube, gently heat the contents of the flask until all the steel is dissolved

and then boil the solution for 30 sec. longer. Remove the tumbler, which will then contain all the sulfur as insoluble cadmium sulfide and add to it 5 c.c. of starch solution and 40 c.c. of 6-normal hydrochloric acid. Titrate at once with the potassium iodate solution to the appearance of a permanent blue color.

6. EVOLUTION METHOD AND ABSORPTION OF HYDROGEN SULFIDE IN BROMINE AND HYDROCHLORIC ACID

Apparatus and Solutions Required

Evolution Apparatus.—Many forms of apparatus have been devised and that shown in Fig. 22 has proved satisfactory.[1]

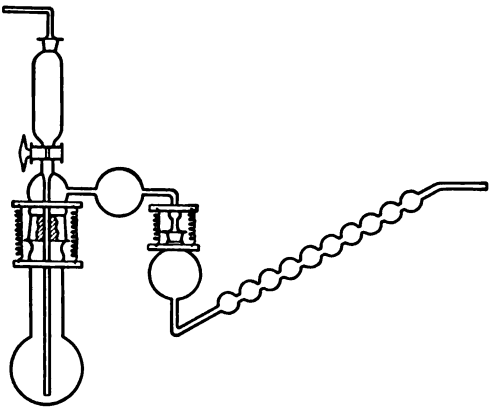


Fig. 22.

Kipp Generator for producing pure carbon-dioxide gas.

Bromine and Hydrochloric Acid.—Add about 13 c.c. of pure bromine, free from sulfate, to 1 liter of hydrochloric acid (d. 1.12), and mix thoroughly by vigorous shaking.

Sodium Chloride Solution.—Prepare a 10 per cent solution of sodium carbonate, free from sulfate, and neutralize with hydrochloric acid.

Procedure.—Weigh out, with an accuracy of 1 cg., about 10 g. of steel into the dry flask of the apparatus shown in Fig. 22. If the material is badly rusted, it is well to add 1 or 2 g. of solid

[1] Can be supplied by Bleckmann and Burger in Berlin.

stannous chloride to avoid any oxidation of the sulfur by ferric chloride.

Fasten the top on the apparatus, which has ground-glass connections, and replace the air in it by introducing a stream of dry carbon dioxide. While doing this, fill the ten-bulb absorption tube with about 30 c.c. of the bromine and hydrochloric acid mixture, using enough to fill all but the last three of the ten bulbs. Connect the tube with the flask and continue passing the stream of carbon dioxide until no more vapors of bromine are visible in the large bulb of the absorption tube. This is usually accomplished in a minute or two.

Then close the stopcock just above the flask, remove the upper end of funnel which serves for the introduction of gas, and add through the funnel the requisite quantity of hydrochloric acid.

For dissolving 10 g. of iron it is best to use 100 c.c. of hydrochloric acid (d. 1.15 to 1.16).[1] To get this concentration of acid, fill the funnel with 50 c.c. of concentrated hydrochloric acid (d. 1.2), and transfer it to the flask with the aid of carbon dioxide pressure. Then add 50 c.c. of hydrochloric acid (d. 1.12), in the same way, avoiding the introduction of any air into the flask.

If the action of the acid is very violent, cool the flask by placing it in a dish of cold water; if it is slow, heat with a small flame.

While the steel is dissolving, stop passing carbon-dioxide gas through the apparatus, in order to avoid driving off too much of the bromine from the absorption tube. The solution of the sample should take place fast enough so that a good current of gas passes through the mixture of bromine and hydrochloric acid. Gradually increase the heating of the flask until finally the liquid in it boils, at which time the entire sample should be dissolved. The dissolving of the steel should not require more than an hour at the most; if more time is required, as in the analysis of some steels containing tungsten or molybdenum, the results are likely to be low.

[1] The use of acid which is more concentrated than this does not give more accurate results. Fuming hydrochloric acid is not suitable because, on heating the flask, too much hydrochloric acid is boiled off and this causes an unnecessary loss of bromine. Moreover, it is more likely to cause the liquid to boil over and sometimes the evolution of the gas is so uneven that bromine vapors are sucked back into the absorption flask, making it necessary to repeat the determination.

When all the iron is dissolved, boil for a minute more, then lead a rapid stream of carbon-dioxide gas through the apparatus, remove the flame from beneath the flask and allow the liquid in it to cool.

After 10 or 15 min., take off the absorption tube and stop the current of carbon dioxide. Rinse the contents of the tube into a porcelain dish, add 2 or 3 c.c. of pure sodium chloride solution and evaporate to dryness on the water bath in an atmosphere free from sulfuric acid fumes. Moisten the residue[1] with hydrochloric acid, add a little water, warm and filter through a small filter into a beaker of about 100-c.c. capacity. Heat the filtrate to boiling and precipitate the sulfuric acid by the slow addition of 5 c.c. of barium-chloride solution (100 g. $BaCl_2 \cdot 2H_2O$ in 500 c.c. water). Stir well and allow to stand in a warm place until the barium sulfate has settled out. Then filter through a small ashless filter, taking the precaution to change the beaker under the funnel before getting the precipitate on the filter, and wash first with very dilute hydrochloric acid and finally with hot water till free from chloride.

Ignite the filter and precipitate very gently until the ash is white and finally over the full heat of the Bunsen burner, with the cover of the crucible off. Do not heat over the blast because of the danger of converting barium sulfate into barium oxide.

On account of the possibility of small quantities of sulfuric acid being present in the reagents and the danger of contamination from the atmosphere (due to the use of sulfuric acid or to the burning of illuminating gas in the laboratory) it is always desirable to carry out a blank determination with the same quantities of reagents and the same operations as in the analysis. Moreover, the evaporation, precipitation, filtration, etc., should take place at the same time the analysis itself is being made. The weight of barium sulfate obtained in the blank experiment should be deducted from that obtained in the analysis. Such blank experiments are desirable in all determinations of relatively small quantities of substances. When the substance determined is

[1] If the material analyzed contains much carbon, the residue obtained at this stage in the analysis often contains bromine substitution products of hydrocarbons. These color the residue and give it a sharp odor but do not affect the analysis in any way.

present in large quantities, as in the determination of sulfur in a nearly pure sulfate, the negative errors due to the solvent action of the reagents upon the precipitate may more than compensate the amount obtained from the reagents.

The solution obtained in the distillation flask after the sulfur has been removed as hydrogen sulfide, may be used for other determinations. It is not suitable for the determination of silicon, however, as there is likelihood of small particles of gelatinous silicic acid adhering to the sides of the flask so firmly that they cannot be easily removed. After rendering all the silicic acid insoluble, by the method described on p. 115, the filtrate may be used for the determination of copper, manganese, nickel, chromium or vanadium.

Computation.—The sulfur content of the steel, when s represents the original weight of the metal and p the weight of the precipitate, is

$$\frac{\mathrm{S} \times p \times 100}{\mathrm{BaSO_4} \times s} = \frac{13.74p}{s} = \text{per cent S}$$

APPLICABILITY OF THE METHODS FOR DETERMINING SULFUR IN IRON AND STEEL

Comparative tests have shown that the rapid evolution methods, when properly carried out, give accurate results with most samples of steel. The time required for carrying out the analysis is short and there is no danger of contamination from sulfur in the laboratory atmosphere. If the acid used is too dilute, or if the solution of the steel takes place too slowly, the results are likely to be a little low. Certain samples of cast iron and some steels contain sulfur in a condition such that it is not evolved as hydrogen sulfide upon treatment with acid. This difficulty can usually be overcome by annealing the sample before analyzing it for sulfur.

The Bamber method is recommended in the United States for settling disputed analyses. The Bureau of Standards, Washington, D. C., have had success with Method *d* although it is open to the theoretical objection that errors are involved, as already pointed out, in precipitating sulfuric acid in the presence of iron.

The first evolution method, Method *a*, gives excellent results but occasionally they are too low. It is slightly more reliable

than the other evolution method because it provides for the oxidation of any gas containing sulfur.

The method based upon the removal of the ferric chloride by ether is probably as reliable as any method that has been proposed but is not used in busy laboratories on account of the time required for the analysis and on account of the unpleasantness and danger involved in constantly working with ether.

Accuracy of the Results.—Duplicate determinations should agree within 0.005 per cent in the analysis of steels containing 0.2 to 0.4 per cent sulfur and within 0.003 per cent in the case of steels containing 0.015 per cent sulfur or less.

7. DETERMINATION OF SULFUR IN INSOLUBLE MATERIALS (*Ferro-silicon, Ferro-chrome, Etc.*)

The mixture of 1 part sodium carbonate and 2 parts magnesium oxide, known as *Eschka's mixture,* is suitable for determining a small sulfur content of an insoluble substance. The sample should be in the form of a fine powder and particular care should be taken to avoid contamination with sulfur in the atmosphere. The use of the gas flame, therefore, is prohibited. An alcohol burner may be used for the ignition but an electric furnace is even better. Ignite the insoluble material in a platinum dish with about eight time as much Eschka's mixture until the oxidation of the sample is complete.

Transfer the ignited mass to a beaker and rinse the dish, using about 50 c.c. of water. Add 15 c.c. of saturated bromine water and boil 5 min. Allow the residue to settle, decant the solution through a filter, boil a second and a third time with 30 c.c. of water, and finally wash the residue with hot water until the filtrate shows no test for chloride. Add 3 c.c. of hydrochloric acid (d. 1.1) and evaporate the solution to dryness to dehydrate silica. Take up the residue with 5 c.c. of hydrochloric acid, dilute, filter and precipitate the sulfuric acid in the filtrate with a hot, dilute solution of barium chloride. Filter, ignite and weigh the precipitate of barium sulfate in the usual manner.

Test Analyses.—The sulfur was determined in a sample of ferro-silicon using a 2-g. sample and 15 g. of the Eschka mixture. Duplicate determinations agreed within 1 mg. of barium sulfate showing respectively 0.037 and 0.044 per cent S.

CHAPTER VII

COPPER

Copper, to the extent of a few tenths of 1 per cent, is a common constituent of iron and steel. Often its presence is accidental but in some cases it is added intentionally for the purpose of preventing corrosion.

1. PRECIPITATION AS SULFIDE FROM ACID SOLUTION

Principle.—The solution containing ferrous chloride and cupric chloride in the presence of free hydrochloric acid is treated with hydrogen sulfide, which precipitates cupric sulfide. The precipitate is purified and the copper determined as oxide.

Procedure.—Dissolve 10 g. of the iron or steel in 100 c.c. of hydrochloric acid (d. 1.12) in a beaker of about 500-c.c. capacity. Heat on the water bath until all the metal is dissolved.

Instead of using a separate sample for this determination, the solution obtained in the determination of sulfur by the evolution method (p. 140) or the filtrate from the silicon determination may be taken.

When the iron is all dissolved, dilute the solution to about 200 c.c.[1] and introduce hydrogen sulfide gas for ½ hr. Then heat a short time on the water bath to expel most of the excess hydrogen sulfide and filter through a filter that runs rapidly. Wash the precipitate and filter with water containing hydrogen sulfide until all the hydrochloric acid has been removed, taking care during all the filtration and washing to keep liquid in the filter. This is important because copper sulfide oxidizes rapidly to copper sulfate on standing in the air and then washes through into the filtrate, causing a turbidity there. It is necessary to remove all the hydrochloric acid from the precipitate because

[1] If the solution stands too long some of the iron is oxidized to the ferric condition which causes the precipitation of sulfur when hydrogen sulfide is introduced.

otherwise some cupric chloride will be lost by volatilization during the next operation.

As soon as the washing is complete, transfer the precipitate to a large, unweighed porcelain crucible and smoke off the filter paper by means of a low flame, keeping the temperature as low as possible. Moisten the ash with concentrated nitric acid and heat again until the carbon is all consumed. To the residue, which now contains all the copper as black cupric oxide, add a few cubic centimeters of hydrochloric acid (d. 1.12) and heat until all the copper oxide is dissolved. Evaporate the solution to dryness, to render traces of silica insoluble, treat the residue with hydrochloric acid, dilute and filter into a small beaker of 100 to 150-c.c. capacity. Wash the filter with water containing a little hydrochloric acid but avoid letting the filtrate exceed about 30 c.c.

To precipitate the copper again, add 10 to 20 c.c. of saturated hydrogen sulfide water and heat on the water bath with frequent stirring until the precipitate collects together and the supernatant liquid is clear. Filter through a small filter until all the hydrochloric acid is removed, using wash water containing hydrogen sulfide. Ignite the precipitate in a weighed porcelain crucible at a low temperature until all the carbon of the filter is consumed, cool in a desiccator and weigh as cupric oxide, CuO.

If care is not taken in igniting the copper sulfide precipitate, there is danger of mechanical loss.

The ignited and weighed cupric oxide should dissolve in hydrochloric acid without leaving a weighable residue; the addition of ammonia in excess should then give a clear, deep-blue solution.

In the analysis of cast iron containing considerable silicon and graphite, the silicon should be removed at the start by Method 1, p. 115, and the copper precipitated as sulfide in the filtrate. The residue obtained after treatment of the silica with sulfuric and hydrofluoric acids should also be examined for copper.

Computation.—If p represents the weight of the copper oxide obtained from a sample of metal weighing s g. then

$$\text{per cent Cu} = \frac{79.89 \times p}{s}$$

2. DETERMINATION AFTER REMOVAL OF IRON WITH ETHER

Principle.—By shaking with ether a hydrochloric acid solution containing considerable ferric chloride and a little cupric chloride, the greater part of the former salt dissolves in the ether while all of the latter salt remains in the aqueous layer.

Procedure.—Dissolve about 10 g. of the sample in dilute nitric acid (d. 1.2) and remove the silicon as described in Method 1 on p. 115. In the filtrate carry out the Rothe ether separation as described under Manganese, p. 73. The aqueous hydrochloric acid solution then contains only a little iron, but all of the copper manganese, nickel, chromium, etc. Evaporate the solution on the water bath to remove dissolved ether, take up the residue in a little hydrochloric acid, add water and filter the solution, if necessary, to remove traces of silica and titanium oxide. Precipitate the copper with hydrogen sulfide according to the procedure given in Method 1, cautiously ignite the precipitate in a porcelain crucible and weigh as cupric oxide, CuO.

3. REMOVAL OF THE IRON WITH SULFURIC ACID[1]

Principle.—In the potential series of the metals, iron has a greater and copper a smaller solution pressure than hydrogen. For this reason iron dissolves readily in dilute sulfuric acid while copper, in the absence of oxidizing agent, does not. To make sure that traces of copper are not dissolved, hydrogen sulfide water should be added to the solution before filtering.

Solutions Required.—*Sulfuric Acid.*—Mix 200 c.c. of concentrated sulfuric acid, d. 1.84, and 800 c.c. of water.

Potassium Ferrocyanide.—Dissolve 10 g. of the crystals in 100 c.c. of distilled water.

Standard Copper Nitrate.—Dissolve 2 g. of pure, electrolytic copper in 20 c.c. of nitric acid (1 vol. conc. acid to 1 of water) and dilute to 1,000 c.c. Each cubic centimeter of this solution contains 0.02 per cent Cu on the basis of a 10-g. sample.

[1] This method is recommended by the U. S. Bureau of Standards, *Circular* No. **14** (1913). The directions given are those authorized by the American Society for Testing Materials.

Procedure.—Dissolve 10 g. of the sample in 75 c.c. of the sulfuric acid and then add 150 c.c. of water. Heat the solution and saturate with hydrogen sulfide. Filter and wash the residue with 1 per cent sulfuric acid containing hydrogen sulfide, till free from iron. Incinerate the paper with its contents in a porcelain crucible and fuse with 0.5 g. of sodium bisulfate (or the potassium salt. Extract the melt with hot water, filter and complete the determination electrolytically in sulfuric acid solution as in Method 4 or colorimetrically as follows:

Evaporate the aqueous solution to about 25 c.c., filter into a 100-c.c. Nessler tube and wash the filter with hot water.

(*a*) If the solution is a strong blue, to another 100-c.c. Nessler tube add 50 c.c. distilled water, 5 c.c. of concentrated ammonium hydroxide solution and the standard copper solution from a burette until the blue colors match.

(*b*) If the solution is a faint blue, add dilute sulfuric acid to faint acidity and then a few drops of the potassium ferro-cyanide solution. To another Nessler tube add 50 c.c. of distilled water, a few drops of ferrocyanide solution and the copper solution from a burette until the reddish brown colors match.

4. ELECTROLYTIC DETERMINATION OF COPPER

Principle.—The first copper sulfide precipitate obtained in Method 1 or in Method 2, as well as the copper sulfate solution obtained in Method 3, may be used for the electrolytic determination of copper. The electrolytic deposition of copper can be accomplished successfully under quite varying conditions. For this reason the procedures described by different chemists often vary considerably. It is well to bear in mind, however, that too much acid prevents the deposition and too strong currents are likely to cause spongy deposits. In general, stronger currents can be employed with a gauze cathode than when a plate electrode is used.

Moreover, the more concentrated the solution and the larger the surface of cathode exposed, the stronger the current may be. Stirring, when accomplished by rotating one of the electrodes, by an electromagnetic effect in Frary's apparatus (p. 179), or in any other way, also shortens the time required for electrolysis by permitting the use of stronger currents.

Procedure.—In case the analysis is started as described in Method 1 or in Method 2, dissolve the ignited cupric oxide, obtained by igniting the sulfide precipitate, in a little nitric acid, add a few drops of sulfuric acid and evaporate until fumes of sulfuric anhydride are evolved. Cool, add enough water to dissolve all the copper sulfate and transfer the solution to a small beaker of not over 200-c.c. capacity.

Dilute this solution, or that obtained in Method 3, to about 50 c.c. and electrolyze with stationary electrodes and a current of about 0.2 ampere or, if a gauze cathode and stirring apparatus are available, a much stronger current may be employed and the analysis finished more quickly.

When all the copper is removed from the solution, which is usually the case at the end of 3 hr. with stationary electrodes, quickly detach the cathode and wash it immediately by plunging it into water in a beaker. Rinse with alcohol, dry a short time at 100°, cool and weigh. Test the solution for copper by passing hydrogen sulfide into it. If any precipitate of copper sulfide is obtained, it may be filtered off, ignited in a porcelain crucible and weighed as cupric oxide, CuO, or the oxide may be dissolved in acid and the solution electrolyzed as before, using a clean electrode surface.

Accuracy of the Results.—With care, the copper content of a steel can be determined by any one of the above methods with an error of not more than 1 mg. in the final weight. Using a 10-g. sample this corresponds to an error of 0.01 per cent. If the quantity of copper in the steel is less than 0.2 per cent duplicate determinations should agree within about 0.005 per cent.

5. THE RAPID DETERMINATION OF COPPER IN STEEL[1]

Principle.—This procedure is a modification of A. H. Low's method[2] for determining copper in ores. Copper is electronegative to aluminium in the potential series of metals and for this reason aluminium displaces copper when placed in the solution of a copper salt. Moreover, copper is lower than hydrogen

[1] KOEPPING, E. D., *J. Ind. Eng. Chem.*, **6**, 696 (1914).
[2] LOW, A. H., "Technical Methods of Ore Analysis."

in the series, so that hydrochloric and sulfuric acids do not dissolve copper in the absence of an oxidizing agent; if any copper dissolves the aluminium will precipitate it even in the presence of acid. The residual copper is dissolved by nitric acid, the solution is neutralized by ammonia, acidified with acetic acid and the cupric ions are changed to cuprous iodide by treatment with potassium iodide whereby an equivalent weight of iodine is set free:

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + 4KC_2H_3O_2 + I_2$$

The free iodine is titrated with standard sodium thiosulfate solution.

Solutions Required.—(1) *Standard Sodium Thiosulfate Solution.*—Dissolve 25 g. of pure, crystallized, sodium thiosulfate $Na_2S_2O_3 \cdot 5H_2O$ in water and dilute the solution to 5 liters. The solution is approximately 0.02-normal. Use water that has been recently boiled free from carbon dioxide and cooled. Standardize the solution against 10 c.c. of tenth-normal potassium permanganate solution (p. 63), against about 0.1 g. of pure iodine (p. 156), or against metallic copper.

To standardize against pure metallic copper, dissolve about 0.1 g. of pure copper,[1] in a 200-c.c. Erlenmeyer flask with 5 c.c. of a mixture of equal parts nitric acid (d. 1.42) and water. Dilute the solution to 25 c.c. and boil a few minutes to remove oxides of nitrogen. To remove the last traces of nitrous acid, add 5 c.c. of bromine water and boil until the excess bromine is expelled. Cool somewhat and add strong ammonia until a slight excess is present. Boil off the excess ammonia and add 7 c.c. of strong acetic acid, which dissolves any copper oxide that may have been deposited by boiling the blue ammoniacal copper solution. Cool to room temperature, add 2 g. of pure potassium iodide, and titrate with sodium thiosulfate until nearly colorless. Then add 2 c.c. of starch solution (0.5 g. of soluble starch dissolved in 25 c.c. of boiling water; the starch solution should cool before using it) and finish the titration.

In making the titration for the first time, it should be borne in mind that cuprous iodide is not white.

[1] This will react with about 80 c.c. of the dilute sodium thiosulfate solution.

The reactions that take place during the standardization may be expressed as follows:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$NO + O = NO_2$$
$$2NO_2 + H_2O = HNO_2 + HNO_3$$
$$HNO_2 + Br_2 + H_2O = HNO_3 + 2HBr$$
$$Cu^{++} + 6NH_3 = Cu(NH_3)_6^{++}$$
$$Cu(NH_3)_6^{++} + 6H^+ = Cu^{++} + 6NH_4^+$$
$$2\,Cu^{++} + 4I^- = Cu_2I_2 + I_2$$
$$2S_2O_3^= + I_2 = S_4O_6^= + 2I^-$$

Procedure.—Weigh from 3 to 10 g. of the metal, according to the probable copper content, into a small beaker and dissolve in 35 c.c. of 6-normal hydrochloric acid (d. 1.12) or sulfuric acid (d. 1.18). Dilute the solution with 35 c.c. of water and introduce a strip of aluminium foil, bent so that it will not lie flat on the bottom of the beaker, and boil the solution for 20 min.

Remove the beaker from the hot plate and wash down the cover glass and sides of the beaker with hot water. Filter through a 11-cm. filter and wash the residue promptly with hot water. Puncture the filter, and rinse the precipitated copper into a 30-c.c. Erlenmeyer flask. Cover the aluminium, in the original beaker in which the copper was deposited, with a mixture of 3 c.c. concentrated nitric acid (d. 1.42) and 7 c.c. of water and pour the acid through the pierced filter. Finally wash the aluminium and the filter with hot water. Boil the copper nitrate solution a few minutes to remove nitrous fumes, cool somewhat, and then add 7 c.c. of strong ammonia (d. 0.90). Boil until the deep blue solution becomes pale blue and the ammonia odor is faint. Add 10 c.c. of 80 per cent acetic acid and boil 1 min. more. Allow the solution to cool and when at the room temperature, or colder, add 3 gr. of potassium iodide and at once titrate the liberated iodine with the sodium thiosulfate solution.

Computation.—If in the standardization of the solution, n_1 c.c. of thiosulfate were required for e_1 g. of copper, then

$$1 \text{ c.c. } Na_2S_2O_3 = \frac{e_1}{n_1} = T \text{ g. copper}$$

If the solution was standardized against 10 c.c. of a-normal permanganate, and n_2 c.c. of thiosulfate were required; then

$$1 \text{ c.c. } Na_2S_2O_3 = \frac{10a \times 0.06357}{n_2} = T \text{ g. copper}$$

If standardized against pure iodine, and e_3 g. of iodine required n_3 c.c. of solution,

$$1 \text{ c.c. } Na_2S_2O_3 = \frac{e_3}{n_3} \frac{0.06357}{0.1269} = T \text{ g. copper}$$

If n c.c. of thiosulfate solution were required in the analysis of s g. of steel, then

$$\text{per cent Cu} = \frac{100n \cdot T}{s}$$

CHAPTER VIII

CHROMIUM

Chromium to some extent, though not usually more than 0.1 per cent, is present in nearly all samples of iron and steel. Special steels are prepared by the addition of chromium, or chromium alloy, to steel; in this way chrome, chrome-nickel, silicon-chrome, chrome-tungsten and chrome-vanadium steels are prepared. In the preparation of these steels, ferro-chrome and chrome-manganese are used chiefly. The chromium content of these two alloys varies considerably.

1. DETERMINATION OF CHROMIUM BY THE BARIUM CARBONATE METHOD[1]

Principle.—The sample is dissolved in 6-normal hydrochloric acid and the resulting solution of ferrous and chromic chlorides is nearly neutralized with sodium carbonate and an excess of barium carbonate added. The chromium is thus precipitated as chromic hydroxide together with a little ferric hydroxide formed by atmospheric oxidation but the greater part of the iron remains in solution as ferrous chloride. The precipitate is fused with sodium carbonate and potassium nitrate. In this way the chromium is oxidized to water-soluble alkali chromate. The aqueous extract is treated with a little hydrogen peroxide, to reduce any permanganate that may have been formed, and the chromium determined either colorimetrically by comparison with a standard sodium chromate solution, or volumetrically by treating with an excess of standard ferrous solution and determining the excess by titration with permanganate.

Solutions Required.—*Hydrochloric Acid*, approximately 6-normal. (See pp. 136, 148.)

Sodium Carbonate.—(See p. 55.)

Barium Carbonate Suspension.—Ten grams in 100 c.c. water.

Standard Sodium Chromate.—Dissolve 6.58 g. of sodium chromate, $Na_2CrO_4.10H_2O$, in 1,000 c.c. of distilled water. One

[1] *Am. Soc. Testing Materials*, **1915**, 222, 233.

cubic centimeter = 0.001 g. Cr = 0.02 per cent Cr when a 5-g. sample is used for analysis.

Standard Potassium Permanganate.—(See p. 158.)

Ferrous Sulfate.—(See p. 158.)

Procedure.—Dissolve 5.00 g. of steel in 50 c.c. of the hydrochloric acid contained in a 300-c.c. Erlenmeyer flask. When the steel is all dissolved, carefully add sodium carbonate solution until nearly all the free acid is neutralized; finish the neutralization with barium carbonate suspension, adding about 1 g. of barium carbonate in excess. Boil the solution gently for 10 or 15 min. with a small watch-glass on the flask, to prevent oxidation of the iron. Filter rapidly through paper and wash the precipitate twice with hot water.[1] Transfer the filter and its contents to a platinum crucible, burn off the paper carefully and fuse the ash with a mixture of 5 g. sodium carbonate and 0.25 g. potassium nitrate. Dissolve the fusion in water, transfer to a beaker and add 2 c.c. of 3 per cent hydrogen peroxide. Boil a few minutes to decompose the excess of peroxide and filter. Complete the determination of the chromium by treating the filtrate by either of the following methods.

1. If the solution is deep yellow in color add 10 c.c. of 18-normal sulfuric acid (1 vol. conc. acid to 1 vol. water) and a measured volume of standard ferrous sulfate solution. Cool thoroughly and titrate with the standard permanganate. The number of cubic centimeters of permanganate used subtracted from the volume of permanganate equivalent to the total ferrous sulfate used, gives the volume of permanganate equivalent to the chromium in the sample. One cubic centimeter of normal $KMnO_4$ = 0.01733 g. chromium. Or, the chromium value of the permanganate may be obtained by multiplying the value of 1 c.c. of permanganate in terms of sodium oxalate by $\frac{2Cr}{3Na_2C_2O_4} = 0.2584$.

2. If the solution is a light yellow, cool and transfer to a 100-c.c. Nessler tube. Then, in another Nessler tube, dilute a carefully measured quantity of standard chromate solution with a measured volume of water until the two solutions appear of

[1] As the ferrous iron in the filtrate oxidizes, a basic ferric salt will precipitate; this precipitate will not contain any chromium.

equal concentration when viewed horizontally. Then, as the concentration of the chromium in one tube is known, it is easy to compute the chromium content in the other tube.

NOTES.—In the titration method it is important that all the hydrogen peroxide be destroyed by boiling the alkaline solution. If left in the solution it will cause the results to come out high. In alkaline solution the peroxide forms sodium peroxide which on boiling decomposes into sodium hydroxide and oxygen.

The above procedure is recommended by the American Society for Testing Materials for the analysis of plain carbon steels. The method recommended for the analysis of alloy steels, which are likely to contain considerably more chromium, is the same in principle except that a 1-g. sample is used, the steel is dissolved in 50 c.c. of sulfuric acid (1:3), the barium carbonate is replaced by magnesium carbonate and the final titration is made with tenth-normal potassium bichromate solution. Several portions of magnesium carbonate are added, taking care that 2 or 3 g. of solid are left undissolved after the boiling is completed. When considerable chromium is present, it is well to titrate directly with freshly standardized, approximately tenth-normal ferrous sulfate solution, using potassium ferricyanide solution (0.1 g. in 50 c.c. water, freshly prepared) as outside indicator; a blue color is obtained as soon as a slight excess of ferrous iron is present. The use of hydrochloric acid to dissolve the alloy steel (a large excess should be avoided) and barium carbonate to precipitate the chromium, is permissible.

2. DETERMINATION OF CHROMIUM BY THE METHOD OF BARBA MODIFIED[1]

Principle.—The chromium is oxidized to chromic acid in sulfuric acid solution by means of potassium permanganate, the excess of the latter is reduced by making the solution ammoniacal and boiling, and the chromium is determined by the ferrous sulfate-permanganate method.

Solutions Required.—*Sulfuric Acid.*—(See p. 151.)

Nitric Acid.—(See p. 92.)

Strong Potassium Permanganate.—(See p. 92.)

Standard Potassium Permanganate.—(See p. 158.)

Ferrous Sulfate.—(See p. 158.)

[1] *Iron Age*, **52**, 153. *Am. Soc. Testing Materials*, **1915**, 236.

Procedure.—Dissolve 1.25 g. of steel in 50 c.c. of the sulfuric acid. If an insoluble residue remains it should be examined for chromium by fusing it with an alkaline flux, as in the preceding method, to see if any chromate is formed. When the steel is all dissolved, add 5 c.c. of the nitric acid and boil till the solution is clear and free from oxides of nitrogen. Dilute with hot water to approximately 150 c.c., heat, and, while boiling, add the strong permanganate solution until a permanent brown precipitate of manganese dioxide is formed. A large excess of permanganate should be avoided, since the manganese dioxide is likely to absorb some of the manganese. Complete the analysis by either one of the following methods:

(*A*) Add 25 c.c. of ammonium hydroxide (d. 0.90) pouring it down the sides of the beaker. Stir well and replace the beaker on a cooler part of the hot plate to avoid "bumping." Stir occasionally and digest about 15 min., or until the permanganate is all decomposed. Add cautiously 20 c.c. of the sulfuric acid and bring to a gentle boil. Then cool the solution to room temperature and transfer to a 250-c.c. flask. Make up to the mark and mix thoroughly by pouring the solution back and forth into a beaker several times. Filter through a dry filter into a dry beaker, rejecting the first few cubic centimeters and use an aliquot part of the filtrate, usually 200 c.c. (= 1 g. of the steel).

Determine the chromium by adding ferrous sulfate and titrating the excess with permanganate (*cf.* p. 158).

(*B*) Add 100 of 6-normal hydrochloric acid and boil until the solution is clear and all the free chlorine is expelled. Cool, dilute to 300 c.c., add a measured quantity of standard ferrous sulfate solution and titrate the excess with permanganate.

3. DETERMINATION OF CHROMIUM BY THE CHLORATE METHOD

Principle.—When an alkali chlorate is added to a fairly concentrated solution of nitric acid, chloric acid is set free which is an energetic oxidizing agent; manganese is oxidized to insoluble dioxide and chromic ions are oxidized to soluble chromic acid:[1]

$$3HClO_3 + Cr^{+++} + H_2O \rightarrow H_2CrO_4 + 3ClO_2 + 3H^+$$

[1] If the concentration of the nitric acid is the same as that recommended in the Ford-Williams method, and considerable chromium is present, the ClO_2 is likely to explode unless the heating is done on a water bath.

Solutions Required.—*Nitric Acid.*—(See p. 57.)

Potassium-ferricyanide Indicator.—Dissolve 0.1 g. of pure potassium ferricyanide in 50 c.c. of distilled water. The indicator solution must be prepared fresh daily.

Standard Potassium Bichromate.—Dissolve 5 g. of the solid in 1,000 c.c. of distilled water and standardize against pure ferrous ammonium sulfate crystals. Since the equivalent weights of ferrous ammonium sulfate and of chromium are 392 and 17.33, the value of 1 c.c. of the solution in terms of ferrous ammonium sulfate multiplied by $17.33/392 = 0.4421$ gives the value in terms of chromium.

Standard Potassium Permanganate.—(See p. 158.)

Standard Ferrous Sulfate.—(See p. 158.)

Procedure.—Weigh 1 g. of steel into a 300-c.c. Erlenmeyer flask and dissolve in 30 c.c. of the nitric acid. Evaporate rapidly to approximately 15 c.c. and add 50 c.c. of concentrated nitric acid, d. 1.42, and 1 g. of sodium chlorate (or potassium chlorate). Evaporate, by boiling, to approximately 30 c.c. and complete the analysis by either of the following procedures:

1. Dilute the solution with 100 c.c. of water, filter off the manganese dioxide using an asbestos filter (*cf.* p. 58) and wash the filter with hot water. Cool the filtrate, dilute with cold water to about 600 c.c. and titrate against the standard ferrous sulfate (the concentration of which has been determined on the same day) using potassium ferricyanide as outside indicator. Or, an excess of the ferrous sulfate solution may be added and the excess determined by titrating back with standard potassium bichromate solution.

2. Proceed exactly as in Method 2, Modification B, p. 153.

4. DETERMINATION OF CHROMIUM BY THE BISMUTHATE METHOD

Principle.—In *cold* solutions containing 20 to 40 per cent of concentrated nitric acid, manganese can be oxidized from the bivalent to heptavalent condition. Chromium is oxidized so slowly under such conditions that, if the solution is promptly filtered, the manganese may be titrated by the ferrous sulfate-permanganate method (*cf.* p. 52). In *hot* solutions permanganic acid in contact with sodium bismuthate is decomposed, usually

forming manganese dioxide, and chromium is oxidized from the trivalent to hexavalent condition. In hot solutions, therefore, chromium can be determined by the ferrous-sulfate-permanganate method, without the manganese doing any harm. Some chemists, in fact, have intentionally added manganese to the solution because manganese dioxide will oxidize chromium.

Procedure.—Dissolve 3 g. of steel, or less if the sample contains more than 1 per cent Cr, in a 250-c.c. Erlenmeyer flask with 50 c.c. of nitric acid (d. 1.13 = 25 per cent conc. acid by vol.). If there is any carbonaceous residue, as in the analysis of cast irons, it should be filtered off and examined for chromium by fusion with an alkaline oxidizing flux (*cf.* p. 151). If the metal is difficultly soluble in nitric acid, it is sometimes necessary to add sulfuric acid to facilitate solution.

When the sample is all dissolved, cool the solution slightly (65 to 75°) and add 2 g. of sodium bismuthate. Agitate a few minutes and then wash down the sides of the flask with a little water. Heat to boiling and boil gently until the permanganate formed from the manganese in the steel is all decomposed as shown by the color; this usually requires about 15 min. Add 50 c.c. of 3 per cent nitric acid (3 c.c. HNO_3, d. 1.42 : 100 c.c. water) and filter off any precipitated manganese dioxide or undissolved sodium bismuthate on an asbestos filter. Wash the residue three times with 50-c.c. portions of the dilute nitric acid. Cool to room temperature by running tap water over the flask and dilute with distilled water to 500 c.c. Add a measured excess of ferrous sulfate solution and titrate the excess with standard permanganate as described on p. 158.

5. DETERMINATION OF CHROMIUM BY THE ETHER METHOD

Principle.—In the trivalent condition, chromium, like manganese, nickel, cobalt and aluminium, may be separated from ferric iron by shaking the hydrochloric acid solution, of suitable concentration, with ether. In the solution which has been freed from the greater part of the iron, the trivalent chromic ions may be oxidized to hexavalent chromic acid ions and the chromium can then be determined either gravimetrically or volumetrically.

Necessary Apparatus and Solutions.—The necessary apparatus and solutions including the Rothe shaking funnel, ether-hydro-

chloric acid solutions, and platinum dish, have already been described under Manganese, p. 71.

According to the method chosen for the final determination of the chromium, various other solutions are necessary. If the chromium is to be determined iodometrically, a standardized tenth-normal solution of sodium thiosulfate is needed; if it is to be determined by the permanganate method, standardized solutions of potassium permanganate and ferrous sulfate are necessary. To determine the chromium gravimetrically, the method to be described requires a solution of mercurous nitrate.

Preparation and Standardization of Tenth-normal Sodium Thiosulfate Solution

Dissolve 124.5 to 125 g. of pure sodium thiosulfate crystals, $Na_2S_2O_3 \cdot 5H_2O$, in water that has been boiled to expel carbonic acid and then cooled. The solution may be standardized against potassium permanganate solution which has been titrated against pure sodium oxalate. The procedure is the same as was described under Manganese, p. 62, for the standardization of permanganate against iodine solution. Another excellent method of standardizing the thiosulfate solution is to titrate it against pure iodine.

To prepare the pure iodine, mix 5 to 6 g. of pure, commercial iodine crystals with 2 g. of potassium iodide,[1] place the mixture in a dry beaker of 150 to 300-c.c. capacity and cover the beaker with a 300-c.c. round-bottomed flask, filled with water at the room temperature. Heat the bottom of the beaker over wire gauze by means of a small gas flame. In a short time the greater part of the iodine will have sublimed from the bottom of the beaker and will have condensed upon the colder bottom of the round-bottomed flask. Scrape the iodine crystals into a fresh beaker and repeat the sublimation without the use of potassium iodide, in order to get a perfectly pure product. Break up the crystals obtained by the second sublimation by pressing them with a pestle in an agate mortar, place them on a watch-glass and dry

[1] The iodide should be free from iodate, as shown by dissolving a little of it and adding a little pure hydrochloric acid; no iodine should be set free to color starch solution.

in a desiccator over calcium chloride for 24 hr.; the top of the desiccator should not be greased.[1]

Place 2 g. of pure potassium iodide and not over 0.5 c.c. of water in a small glass-stoppered weighing tube and weigh carefully to 0.1 mg. Open the stopper and introduce about 0.5 g. of the purified and dried iodine, which dissolves quickly in the concentrated potassium iodide solution, insert the stopper and weigh again.

Hold the weighing tube over a 500-c.c. Erlenmeyer flask containing about 1 g. of pure potassium iodide dissolved in 200 c.c. of water. Open the stopper of the weighing tube and at once drop the tube and its contents into the dilute potassium iodide solution. In this way there is no chance of losing an appreciable quantity of iodine by vaporization. Titrate the iodine with tenth-normal sodium thiosulfate until the iodine color fades to a pale yellow, then add 2 c.c. of freshly prepared starch solution[2] and continue adding the sodium thiosulfate solution, drop by drop, till the blue color just disappears.

During the titration, the following reaction takes place:

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

If the sodium thiosulfate solution is exactly tenth-normal, 1 liter of it will react with exactly one-tenth the atomic weight of iodine, or 1 c.c. is equivalent to 0.01269 g. iodine. It is usually not worth while to make the solution exactly tenth-normal. By dividing the weight of iodine neutralized by 1 c.c. by 0.1269, the relation of the solution to the normal solution can be obtained and this value may be called the *normality* of the solution. The inconvenience resulting from the use of such a fraction is very slight.

The reaction between the chromate and iodide ions in acid solution may be expressed as follows:

$$2CrO_4^{=} + 6I^- + 16H^+ = 2Cr^{+++} + 8H_2O + 3I_2$$

This equation shows that 1 atom of chromium is equivalent to 3 atoms of iodine or 1 c.c. of normal sodium thiosulfate

[1] Grease is likely to be attacked by the iodine vapor forming hydriodic acid which may contaminate the iodine crystals.

[2] The starch solution is prepared by dissolving 0.5 g. of soluble starch in 25 c.c. of hot water. It is ready for use as soon as it cools.

solution is equivalent to 0.01733 g. of Cr. By multiplying this last value by the value expressing the relation of the sodium thiosulfate solution to the normal solution, *i.e.*, its normality, the value of 1 c.c. of the thiosulfate solution in terms of chromium is obtained.

Preparation and Standardization of Permanganate and Ferrous Sulfate Solutions.—A suitable solution of permanganate may be prepared by dissolving about 16 g. of potassium permanganate in 5 liters of water. The preparation and standardization of such a solution was discussed under Manganese, p. 61.

To prepare a ferrous sulfate solution of corresponding concentration, dissolve 60 g. of pure ferrous sulfate crystals, $FeSO_4 \cdot 7H_2O$ in water, add 100 c.c. of concentrated sulfuric acid, and dilute to 2 liters.

The ferrous sulfate solution is not very stable but gradually weakens owing to the slow oxidation of the ferrous ions. For this reason, its strength compared with that of the permanganate must be determined on the same day that the analysis for chromium is made. Measure out a portion of the solution by means of a pipette, dilute to 100 c.c. and titrate with permanganate. Use the same quantity of ferrous sulfate as in the analysis for chromium. The quantity chosen must be sufficient to react with all the chromium present so that an excess remains to be titrated with permanganate. Then, by subtracting the volume of permanganate used in titrating the excess of ferrous sulfate in an analysis, from the volume of permanganate which has been found to be required for all of the ferrous sulfate used, the difference gives the volume of permanganate which is equivalent to the chromium in the sample.

The reaction between the chromate and ferrous ions may be expressed as follows:

$$CrO_4^{--} + 3Fe^{++} + 8H^+ = Cr^{+++} + 3Fe^{+++} + 4H_2O$$

The reaction between ferrous and permanganate ions is:

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O$$

Since the change in valence of the chromium is three, it is clear that 1 c.c. of normal permanganate is equivalent to $\frac{Cr}{3{,}000} =$ 733 g. Cr, as in the titration with sodium thiosulfate.

In the standardization of the permanganate against sodium oxalate the reaction is

$$5C_2O_4^{--} + 2MnO_4^- + 16H^+ = 10CO_2 + 2Mn^{++} + 8H_2O$$

If n c.c. of permanganate are used in titrating p g. of sodium oxalate then the normality of the permanganate solution is

$$\frac{p}{n \cdot \frac{Na_2C_2O_4}{2{,}000}} = \frac{p}{0.067n}$$

and the value of 1 c.c. permanganate in terms of chromium is

$$\frac{0.01733 \times p}{0.067n} = \frac{p}{n} 0.2587 \text{ g. Cr}$$

Mercurous Nitrate Solution.—Pulverize 100 g. of pure mercurous nitrate and shake it with water in a glass-stoppered liter bottle.

To prevent oxidation, add a little pure mercury. The mercurous nitrate is hydrolyzed to some extent so that the solution always contains free acid and some basic mercurous nitrate remains at the bottom of the bottle.

Procedure.—Of pig iron and steel with low chromium content take 10 to 15 g., of richer materials 4 to 5 g. Dissolve the sample in a porcelain dish with dilute nitric acid[1] (d. 1.2), evaporate to dryness, destroy the nitrates, take up with hydrochloric acid and remove the silica as in Method 3, p. 121.[2]

The silica frequently holds back a little chromium. After volatilizing the silica with sulfuric and hydrofluoric acids, therefore, test for chromium. Mix it in the platinum crucible with a little magnesia-sodium-carbonate mixture (*cf.* p. 125) and heat strongly for ½ hr. Extract the product obtained with hot water to dissolve the sodium chromate. Filter off the residue and acidify the filtrate with hydrochloric acid. Add about 0.25 g. of potassium iodide and titrate any liberated iodine with the tenth-normal sodium thiosulfate solution. Instead of titrating the

[1] Some samples of materials rich in chromium do not dissolve readily in nitric acid; in such cases concentrated hydrochloric acid, without the use of an oxidizing agent, may be used. If this dissolves the sample, evaporate to dryness, remove the silica by Method 1, p. 115, oxidize the iron with nitric acid and prepare for the ether separation in the usual way.

[2] To hasten the process, the procedure described on p. 88, may be used.

sodium chromate, it can be treated as described on p. 162 and the chromium weighed as oxide.

Evaporate the filtrate from the silica, and shake with ether as described on p. 73.

Precipitate the copper as sulfide from the hydrochloric acid solution and in the filtrate carry out the treatment with caustic soda and sodium peroxide as described on p. 76.

Treat the fusion in the platinum dish with water; all the chromium goes into solution as sodium chromate and part of the manganese dissolves as sodium manganate, imparting a green color to the solution. In case the excess of sodium peroxide used is insufficient to convert the manganese to manganese dioxide on boiling the solution,[1] add one or two knife-bladefuls more of this reagent, stir well and cover with a watch-glass.

Transfer the solution to a 300-c.c. beaker, dilute with water to about 200 c.c., and allow the precipitate to settle while heating on the water bath. Cool, filter the clear solution, which is colored more or less yellow according to the quantity of chromium present, and wash the precipitate, which contains all the manganese, nickel, cobalt and residual iron, with hot water until the washings are no longer alkaline to litmus. The precipitate may be used for the determination of manganese, nickel and cobalt. The aqueous solution may contain besides sodium chromate, some sodium phosphate and sodium vanadate according to the extent that these elements are present in the original material. If vanadate is present it interferes somewhat with the iodometric determination of the chromium, as it is reduced slowly by means of hydriodic acid. It is hard to get a good end-point with sodium thiosulfate and the results for chromium are too high.

It is also claimed that vanadic acid influences the volumetric estimation of the chromium when ferrous sulfate and potassium permanganate are used in the titration, though Campagne has shown that good results can be obtained in the presence of vanadium.

It is safer to remove the vanadium before attempting to titrate the chromium.

By treating the aqueous solution with mercurous nitrate

[1] In such cases purple permanganate ions are usually present.

solution, mercurous chromate, phosphate and vanadate are precipitated.

To recover the chromium in it, this precipitate must be filtered off, the filter and precipitate ignited, the mercury volatilized and the residue subjected to a suitable fusion process (*cf.* pp. 76, 163, 165).

If the chromate solution shows only a slight pale yellow color, the whole of it may be taken for the chromium titration. If much chromium is present, as shown by a deep yellow color, transfer the solution to a 500-c.c. calibrated flask and take an aliquot part, *e.g.*, 50 c.c. for the titration.

It is not advisable to attempt to titrate more than 0.1 g. of chromium or the solutions, toward the end of the titration, will become so green with chromic ions that it is difficult to detect the correct end-point. This is true whether the determination is carried out by the iodometric method or by means of ferrous sulfate and permanganate. When strongly colored, it is necessary to dilute largely before titrating.

(α) *Iodometric Determination of Chromium.*—Before acidifying the alkaline chromate solution, it is necessary to decompose the excess sodium peroxide by boiling. If any of it is left undecomposed, hydrogen peroxide is formed on making the solution acid. This may unite with the chromic acid to form blue perchromic acid which is not very stable and decomposes readily into chromic salt. Some of the chromium, therefore, is likely to miss the titration if any hydrogen peroxide is formed. After decomposing all the excess of sodium peroxide, transfer the solution to a 600-c.c. Erlenmeyer flask, acidify the cold solution with hydrochloric acid, and add 1 g. of pure potassium iodide, which must be free from iodate.[1] Dilute to about 200 to 300 c.c. and titrate with thiosulfate solution until the iodine color fades to a pale yellow, then add 2 c.c. of starch solution and titrate till the blue color just disappears.

Computation.—If in the analysis of s g. of material, n c.c. of f-normal thiosulfate solution were used, including that required for titrating the chromium found in the residue from the silica, then

$$\text{per cent Cr} = 1.733\, f\frac{n}{s}$$

[1] *cf.* pp. 63, 156.

The value f, as described on p. 55, is obtained by dividing the value of 1 c.c. of the sodium thiosulfate solution in terms of the substance against which it is standardized by the value of 1 c.c. of a *normal* solution of sodium thiosulfate in terms of the same substance.

(β) *Titration with Ferrous Sulfate and Permanganate.*—To the chromate solution freed from excess of sodium peroxide, as in Method α, add dilute sulfuric acid (1:10) in moderate excess and dilute the solution to about 300 c.c. Add, by means of a pipette, 25 or 50 c.c. of ferrous sulfate solution. Enough ferrous sulfate must be used to reduce all of the yellow chromate ion to green chromic ion. If more than 50 c.c. are required to accomplish this reduction, it is advisable to work with a smaller sample, obtained by taking an aliquot part of the solution as already described.

Then, without allowing the solution to stand very long, titrate slowly with permanganate. Titrate a fresh portion of the ferrous sulfate solution alone against the permanganate, using the same pipette that was used in the analysis.

Computation.—If a c.c. of f-normal permanganate were used in titrating a pipetteful of ferrous sulfate and b c.c. of permanganate were used in the analysis of s g. of material, then

$$\text{per cent Cr} = \frac{1.733 f (a - b)}{s}$$

or, if T represents the value of 1 c.c. permanganate in terms of chromium (pp. 158, 159).

$$\text{per cent Cr} = \frac{100 T (a - b)}{s}$$

(γ) *Precipitation with Mercurous Nitrate Solution.*—For the chromium determination use all or a part of the filtrate from the fusion with sodium peroxide (p. 160) according to the amount of chromium present.

Transfer the solution to a 300 to 400-c.c. beaker and cautiously neutralize it with dilute nitric acid. Stop adding the acid as soon as a piece of litmus paper in the solution assumes a wine-red color. Then add mercurous nitrate solution, cover the beaker with a watch-glass and boil the solution a short time. Allow the precipitate, which is gray or grayish green when thrown down

from faintly alkaline solutions, and red (or yellow) when thrown down from faintly acid solutions, to settle to the bottom of the beaker and test with more mercurous nitrate solution to see if the precipitation is complete.

The mercurous nitrate solution is always slightly acid as a result of the hydrolysis, so that, when much of the reagent is added, the solution may become so acid that the precipitation of the chromic acid is incomplete. In such cases a few drops of ammonia may be added and the solution again heated. This must be done with caution, for an excess of ammonia will cause the formation of soluble ammonium chromate and the precipitation of the chromic acid will be incomplete. After the precipitate has settled, test again with a little more mercurous nitrate solution. Filter off the precipitate through an ashless filter paper and wash it first with pure water and finally with very dilute mercurous nitrate solution (25 c.c. of the reagent diluted to 500 c.c.). If it is intended to purify the precipitate, it is not necessary to wash it entirely free from alkali salts.

Ignite the filter together with the precipitate in an open platinum crucible under a good hood (on account of the poisonous vapors) and finally heat strongly. Sometimes the ignited chromic oxide, Cr_2O_3, which is formed by the ignition of the mercurous chromate, is pure enough to weigh. This is seldom the case in the analysis of steel. Of the elements likely to be present in steel, mercurous nitrate solution will precipitate the phosphorus as phosphate, the vanadium as vanadate, the tungsten as tungstate, and the molybdenum as molybdate. Of these elements, phosphorus and vanadium are the only ones that need be considered. The tungstic acid will be precipitated practically completely with the silica and will be left as a yellow residue after the volatilization of the silicon as fluoride. Molybdenum follows the iron in the ether separation so that very little of it can be present at this stage in the analysis. The method of purifying the precipitate, however, would serve equally well for separating chromium from phosphorus, vanadium, tungsten and molybdenum.

Purification of the Impure Chromic Oxide.—The purification process to be described depends upon the fact that it is possible by means of an alkaline reducing fusion to keep the chromium

as insoluble chromic oxide while converting the impurities into soluble alkali salts. A suitable flux is prepared by mixing 4 parts of pure double carbonate of sodium and potassium with 1 part of pure potassium acid tartrate. Instead of the double carbonate, sodium carbonate may be used. (Another suitable flux may be prepared with sodium carbonate and sodium acetate.)

Commercial potassium acid tartrate (cream of tartar) is likely to contain a little calcium sulfate. In case pure potassium acid tartrate is not at hand, it may be prepared by adding a filtered solution of 150 g. of tartaric acid to an aqueous solution of 56 g. of pure caustic potash. Cool the solution, filter off the crystals with the aid of suction, and dry them at 105° in the hot closet

Mix the impure chromic oxide in the platinum crucible with 8 to 10 times as much of the carbonate-tartrate mixture and heat with a moderate flame. The potassium acid tartrate soon begins to decompose. Raise the cover of the crucible and watch the carbonization and fusing together of the contents. The carbon that is deposited from the tartrate gradually oxidizes to carbonic oxide gas in the fusion mixture. As soon as nearly all of the free carbon is gone, stop fusing.

Special attention must be paid to the proper timing of the fusion. If it is continued too long, some of the chromic oxide will be oxidized to chromate, imparting a yellow color to the fusion. If the fusion is not continued long enough, some of the impurities may not be converted to soluble alkali salts.

If considerable chromic oxide is to be purified, it is rather better to fuse it first with pure sodium carbonate and then reduce the chromate by the addition of potassium acid tartrate finishing the treatment as described.

After cooling, place the crucible in a small beaker and warm the melt with a little water. When all of the alkali salts have dissolved, remove the crucible, washing it well with hot water, and filter the solution through an ashless filter. Chromic oxide, mixed with some charcoal, remains behind upon the filter. Wash the filter and precipitate thoroughly with hot water and finally with a few drops of very dilute nitric acid, to make sure that all the alkali salts are dissolved. Ignite the precipitate in a platinum crucible and weigh the green chromic oxide, Cr_2O_3.

If desired, the purity of the chromic oxide may be verified by fusing it with magnesia-sodium-carbonate mixture (p. 125) dissolving the sodium chromate in water and titrating the chromate in acid solution by either Method α or Method β.

The filtrate from the fusion for the purification of the chromic oxide may be used for the determination of phosphorus or of vanadium.

Computation.—If p g. of chromic oxide were obtained in the analysis of a sample weighing s g. then

$$\text{per cent Cr} = \frac{2\ \text{Cr} \times p \times 100}{\text{Cr}_2\text{O}_3 \times s} = \frac{68.42p}{s}$$

The chromium carried down by the silica must also be taken into consideration (p. 159).

6. DETERMINATION OF CHROMIUM BY FUSION OF THE OXIDES WITH SODIUM PEROXIDE

Principle.—The sample is converted into oxide and the chromic oxide is converted to chromate by fusing with sodium peroxide in a nickel or iron crucible. The method is suitable for chrome-steel, chrome-nickel steel, chrome-tungsten steel and chrome-vanadium steel; steels with low-chromium content are analyzed preferably by one of the methods already described, using a larger sample.

Procedure.—Treat 2 g. of the metal in a small porcelain evaporating dish with 6-normal nitric acid (d. 1.2) evaporate the solution to dryness, and heat the residue until the nitrates are decomposed, keeping the dish covered with a watch-glass to prevent loss by spattering. During the heating, the oxides are dislodged, for the most part, from the sides of the dish. Transfer the loose particles to an agate mortar, mix them with sodium peroxide (about 16 g. is used in an analysis) and transfer the mixture to a well-scoured nickel or iron crucible.[1] Carefully scrape off with a spatula as much as possible of the oxide from the porcelain dish, mix it with sodium peroxide and add the mixture to the crucible. Next place a little sodium peroxide in the

[1] A new iron crucible is usually covered with some sort of varnish. To remove it, heat the crucible to redness over a Méker burner or a blast lamp and plunge the red hot crucible into water.

dish, rub the dish with it and transfer to the crucible. Finally add a little caustic soda solution to the dish, heat it nearly to boiling and rinse the solution into a beaker, setting it aside for the time being.

Cover the crucible and heat it with a small flame until the mass melts, then raise the temperature and heat to dull redness for about 15 min. Allow the crucible to cool, place it in a beaker, add hot water, and cover the beaker with a watch-glass. The mass dissolves quickly with decomposition of most of the excess of peroxide. Add the reserved alkali solution with which the evaporating dish was washed, remove the crucible, washing it thoroughly, and allow the beaker and its contents to stand an hour or two on the steam bath. If the solution should not be yellow but green in color, owing to the presence of manganate, add a little sodium peroxide and stir; this serves to reduce the manganate to manganese dioxide. Dilute the solution to 200 c.c., allow it to cool and, when well settled, decant the supernatant liquid through a filter, without disturbing the residue. Cover the residue with hot water and allow it to settle again. Then filter as before, catching the filtrate in a fresh beaker so that if any of it runs through turbid it will not be necessary to refilter the entire filtrate. Transfer the residue to the filter and wash it with hot water until the washings are neutral to red litmus paper.

A little chromium is likely to remain with the iron in an insoluble condition such that it is impossible to remove it by washing. To recover this chromium, ignite the precipitate and filter and repeat the fusion with sodium peroxide in exactly the same manner as before, finally combining the aqueous extract of the fusion with that first obtained.

Boil the solution until all the excess of sodium peroxide is destroyed, cool to room temperature and dilute up to the mark in a 500 c.c. calibrated flask. Use an aliquot part, usually one-fifth, for the determination of the chromium according to p. 161.

If preferred, the aqueous, alkaline solution of sodium chromate may be used for the gravimetric determination of chromium according to p. 162. In that case, treat the impure chromic oxide with sulfuric and hydrofluoric acids and heat to expel any silica, before fusing it with the alkaline reducing flux.

7. DETERMINATION OF CHROMIUM IN MATERIALS INSOLUBLE IN ACID

The method is applicable to the analysis of ferro-chrome, chrome-tungsten steel, etc.

Procedure.—Intimately mix from 0.5 to 2 g. of the pulverized sample with 10 times as much of the Rothe fusion mixture (p. 125), transfer the mixture to a platinum crucible, and heat ½ hr. over a Tirrill burner and the same length of time over a large Méker burner, or over a blast lamp. Transfer as much as possible of the ignited product to an agate mortar, moisten it with a little water and crush it carefully to a paste. Rinse the paste into a beaker and heat on the steam bath to extract the soluble chromate. Allow the residue to settle, decant the solution through a filter, and wash the residue by decantation and then thoroughly on the filter, with hot water. Ignite the filter and residue in the platinum crucible and fuse it with about four times as much sodium carbonate as the original sample weighed. After cooling the crucible, extract the soluble sodium salts and repeat the fusion with sodium carbonate in order to remove the last traces of chromium. If the material was sufficiently fine, the quantity of chromium left in the residue after the third fusion is perfectly negligible.

The residue may be used for the determination of iron, manganese, or nickel.

Combine all the aqueous extracts and dilute to 500 or 1,000 c.c. in a calibrated flask. Take an aliquot part for the chromium determination, according to p. 161, bearing in mind that the solution may contain vanadate or tungstate of sodium.

Test Analysis.—(1) *Separation of Chromium and Iron by the Ether Method.*—Ten cubic centimeters of a solution of chromic chloride was analyzed by the permanganate process and found equivalent to 53.5 c.c. of permanganate (= 0.1083 g. Cr).

In duplicate experiments, 10 c.c. of the chromic chloride solution were mixed with 50 c.c. of pure ferric chloride solution (= 4.4 g. Fe), the iron removed by the ether method and the chromium determined by Method 5β, p. 162. In one experiment 53.5 c.c. of permanganate were used and in the other 53.3 corresponding to 0.1083 and 0.1079 g. Cr; this shows that the separation is accurate within the usual limits of error.

Two experiments were carried out with respectively 5 and 10 c.c. of another chromic chloride solution (= 0.0031 and 0.0062 g. Cr) in the presence of ferric chloride solution corresponding to 3.2 g. Fe. In this case the analysis was finished by titration with sodium thiosulfate solution and the values agreed perfectly to the two significant figures given above, showing that with low chromium the process gives results agreeing within 0.0001 g. of chromium.

2. *Analysis of Various Chrome Steels.*—A sample of chrome steel weighing 6.000 g. was analyzed by Method 5 and one-fifth of the solution was taken for the final determination. Volumetrically, by the permanganate method, the value 4.07 per cent Cr was obtained which agreed well with 4.05 per cent Cr, the value obtained gravimetrically.

A sample of nickel-chrome steel, weighing 6 g., was analyzed by the sodium thiosulfate method, using two-fifths of the original solution, and the value 0.22 per cent Cr was obtained. Another test was carried out with a 6-g. portion of the steel and using the entire solution for the final titration. In this case the value 0.23 per cent Cr was obtained.

A sample of chrome-tungsten steel with 6 per cent tungsten, analyzed by Method 5β, gave 5.82 per cent Cr and by Method 5α, 5.84 per cent Cr. In this case 0.04 per cent Cr was recovered from the silica.

A sample of chrome-tungsten steel with 4 per cent W, analyzed by Method 5β, showed 10.22 per cent Cr and by Method 5α, 10.36 per cent Cr. In this case the chromium from the silica in Method 5β in one case amounted to 1.06 per cent.

A sample of ferro-chrome was analyzed by Method 7. One gram of the substance was weighed out and one-tenth of the solution taken for the final titration with sodium thiosulfate. In duplicate determinations the values 60.8 and 60.7 per cent Cr were obtained.

3. *Purification of Chromic Oxide Precipitates.*—Ten cubic centimeters of tungstate solution (0.2724 g. WO_3) were mixed with 10 c.c. of chromate solution (0.0250 g. Cr_2O_3) and the solution precipitated with mercurous nitrate. After purification with the potassium acid tartrate mixture, the Cr_2O_3 obtained weighed 0.0252 g.

A similar experiment with vanadate solution (0.153 g. V_2O_3) and chromate solution (0.0500 g. Cr_2O_3) gave 0.0505 g. of purified Cr_2O_3.

Accuracy of the Results and Permissible Variations.—With chromium content of less than 0.5 per cent duplicate determinations should agree within 0.005 per cent and with 10 per cent Cr, or more, the values should agree within 0.1 per cent. The values should also closely approximate the truth.

CHAPTER IX

IRON

In the analysis of a sample of ordinary steel the percentage of iron is usually determined most accurately by deducting the percentages of other constituents from 100. In the analysis of special steels and ferro alloys, however, it is often important to have an accurate and rapid method for determining the iron directly. A great many methods are known for the accurate determination of iron but unfortunately nearly all of them are influenced by some of the other elements which are found in steel alloys. For this reason it is hard to give general directions which will be applicable in all cases and sometimes the errors involved in separating iron from a number of possible interfering elements are such as to influence seriously the final determination.

Thus the small amount of carbon present in the iron wire that is so frequently used for standardization may influence the volumetric determination to the extent of several tenths of 1 per cent, unless special precautions are taken, such as gently boiling the solution or oxidizing with strong permanganate before attempting to reduce the solution previous to the titration with permanganate. Similarly, the errors in the gravimetric determination of iron are often considerable. Thus vanadium, titanium, aluminium and molybdenum may be precipitated with ferric oxide and the ammonia used may contain dissolved silica which will be precipitated when poured into the acid solution and thus contaminate the ferric hydroxide precipitate. Moreover, there is difficulty in igniting the ferric oxide; if it is heated too hot, especially when all the carbon is not consumed, some magnetic oxide is formed, and if the precipitate is not washed free from chloride some ferric chloride may be volatilized.

1. DETERMINATION OF IRON IN MATERIALS SOLUBLE IN ACID

(A) MOHR'S IODOMETRIC METHOD

The method depends upon the reduction of the iron with

potassium iodide in slightly acid solution and the titration of the liberated iodine with sodium thio-sulfate.

$$2Fe^{+++} + 2I^- \rightarrow_1 2Fe^{++} + I_2$$
$$I_2 + 2S_2O_3^{--} \rightarrow S_4O_6^{--} + 2I^-$$

The determination of the iron can usually be combined with the determination of some other constituent. Thus the ether solution obtained in the determination of manganese, chromium, nickel and cobalt, aluminium, titanium, vanadium, etc., may be used for the iron determination. If an ethereal solution of ferric chloride is exposed to the light, particularly direct sunlight, for any length of time, some of the ferric chloride becomes reduced to ferrous chloride. In such cases the solution should be oxidized and the excess of oxidizing agent removed before attempting to determine the iron by the iodometric process.

Shake the ethereal solution in the Rothe shaking funnel with several portions of water, transferring the washings to a tall beaker, then wash a few times with dilute hydrochloric acid, until finally the addition of a fresh portion of hydrochloric acid shows no further yellow color of dissolved ferric chloride and the upper ether layer is perfectly colorless. Evaporate off the dissolved ether by heating on the water bath and concentrate to a small volume.

Dilute the solution to 500 c.c. in a calibrated flask, mix thoroughly, and take an aliquot portion corresponding to about 0.25 g. of iron.

Pour the slightly acid solution into a 300-c.c. Erlenmeyer flask, add 3 g. of pure potassium iodide, free from iodate, and titrate the liberated iodine with tenth-normal thiosulfate solution. Add the thiosulfate slowly from the burette until only a slight color remains in the iron solution, then add 2 c.c. of starch solution (*cf.* p. 63) and titrate until the blue color disappears. When completely decolorized, the blue color may return after a little while on account of the fact that the last traces of ferric chloride are reduced very slowly by hydriodic acid at the room temperature. To hasten this decomposition, heat the solution to 50°, or 60° at the most; in a short time all of the iron will be reduced to the ferrous condition. Cool the flask under the water tap and finish the titration with sodium thiosulfate, adding a little more starch.

To the amount of iron thus obtained, a correction must be added corresponding to the iron remaining in the aqueous layer after treatment with ether and also for that remaining with the silica and obtained as ferric oxide after the volatilization of the silicon fluoride. Fuse this residue with a little sodium carbonate and dissolve the melt in a little dilute hydrochloric acid, setting aside the solution. In the aqueous solution obtained after the ether separation, precipitate the iron as basic ferric acetate, by neutralizing the solution with ammonia, making acid with acetic acid and boiling the dilute solution with 3 g. of ammonium acetate. Dissolve the precipitate in hydrochloric acid and add the solution to the iron solution obtained from the silica residue. Evaporate off the excess of acid and carry out the iodometric determination of the iron.

Instead of taking the ethereal solution of ferric chloride, the solution remaining in the flask after the evolution method for determining sulfur (p. 140) may be used, or the solution obtained after the determination of copper (p. 143). After the removal of the copper, which is always necessary when appreciable amounts of copper are present because cupric salts react with potassium iodide (*cf.* p. 147), concentrate the solution by evaporation and carefully oxidize the iron by adding nitric acid, drop by drop, or potassium chlorate (about 4 g. for 10 g. of iron). Evaporate the solution with concentrated hydrochloric acid to remove the excess of oxidizing agent and carry out the iodometric determination in an aliquot part of the diluted solution.

Computation.—Assuming that n c.c. of f-normal sodium thiosulfate were used in titrating the iron in a sample representing s g. of the original material, then

$$\text{per cent Fe} = \frac{n \times f \times 5.585}{s}$$

(B) Zimmermann-Reinhardt Method

Procedure.—In an aliquot portion of the original solution, obtained as described in the above method, determine the iron by titration with permanganate solution after reducing with stannous chloride, removing the excess of stannous chloride with mercuric chloride and adding manganous sulfate and phosphoric acid solution exactly as described on p. 232 for the standardization of a ferric chloride solution.

2. DETERMINATION OF IRON IN INSOLUBLE MATERIALS

Procedure.—Fuse the finely pulverized material with magnesia-sodium-carbonate mixture in a platinum crucible as described on p. 85. Extract the melt with hot water, whereby chromate, vanadate and other substances that may interfere are dissolved in the form of sodium salts of the corresponding acids, and the iron remains behind as insoluble ferric oxide. Wash the residue thoroughly and determine the iron by either of the above volumetric methods.

If the original material contained no appreciable amount of disturbing substances such as chromium, vanadium or molybdenum, the fusion may be dissolved at once in dilute hydrochloric acid and the solution used for the titration.

If copper is present to an appreciable extent, the acid solution should be saturated with hydrogen sulfide, the copper sulfide precipitate filtered off and the iron determined in the filtrate as described on p. 172.

With materials rich in titanium, the fused product obtained after ignition with magnesia-sodium-carbonate mixture should be dissolved directly with concentrated hydrochloric acid (d. 1.2) or, if it is desired to remove the soluble sodium salts, the melt should be extracted with *cold* and not hot water as otherwise it is difficult to get a clear solution with hydrochloric acid. Any pertitanic acid that may form during the solution of the melt will be reduced during the subsequent evaporation.[1] In this case the iodometric method should be used, or the iron should be reduced with hydrogen sulfide (*cf.* p. 239).

Test Analyses.—(*a*) *Determination of Iron in 23 Per Cent Nickel Steel.*—Using samples weighing 0.5 g. and carrying out the ether separation and titration with sodium thiosulfate, the results obtained in duplicate experiments were 75.6 and 75.6 per cent Fe.

(*b*) *Iron in Ferro-vanadium with 25.7 Per Cent V.*—Using 4.0-g. samples and one-twentieth of the solution for the final titration, the values obtained were 71.5 and 71.6 per cent Fe.

(*c*) *Iron in 50 Per Cent Ferro-vanadium, Rich in Carbon.*—The results obtained in duplicate experiments using the ether

[1] KNECHT and HIBBERT, *J. Soc. Chem. Ind.*, **30**, 396.

separation and sodium thiosulfate titration were 31.2 and 31.0 per cent Fe.

In another experiment the sample was fused with magnesia-sodium-carbonate mixture and the sodium thiosulfate titration showed 31.3 per cent Fe.

(*d*) *Iron Phosphide with* 24.9 *Per Cent P.*—Using 1.0 and 0.51-g. samples and taking three-tenths of the solution for the titration after the fusion with magnesia-sodium carbonate, the results obtained were 74.5 and 74.7 per cent Fe.

(*e*) *Titanium Metal,* 63 *Per Cent Pure.*—Experiments with the fusion method, followed by sodium thiosulfate titration, gave the values 2.99 and 3.05 per cent Fe.

Accuracy of the Method and Permissible Deviation in the Values

If the iodometric method for the determination of the iron is carefully carried out, the following agreement of the results can be obtained.

Iron Content	Permissible Deviation
0.1 to 0.5 per cent	0.02
0.5 to 2.0 per cent	0.03
2.0 to 10.0 per cent	0.05
10.0 to 25.0 per cent	0.10
25.0 to 50.0 per cent	0.15
50.0 to 100.0 per cent	0.20

CHAPTER X

NICKEL

Nickel, in traces at least, is a very common constituent of iron and steel. It is rarely present much in excess of 0.1 per cent except when it is intentionally added in special steels.

Three methods for the determination of this element will be described, the dimethylglyoxime method, the electrolytic method, and the volumetric method. Of these methods only the first mentioned is uninfluenced by the presence of cobalt which almost invariably accompanies nickel. Usually the cobalt content is in the neighborhood of 1 per cent of the nickel content; the results obtained by the last two methods should be correspondingly higher.

1. DETERMINATION OF NICKEL BY THE DIMETHYLGLYOXIME METHOD

Principle.—From a nearly neutral solution, it is possible to precipitate nickel quantitatively by the addition of dimethylglyoxime[1] in alcoholic solution. The method was first used by Tschugaeff[2] for the qualitative detection of traces of nickel and was perfected by Brunck for quantitative work.[3] Dimethylglyoxime, also called *diacetyldioxime*, has the following constitutional formula:

$$\begin{array}{ccccccc} CH_3 & - & C & - & C & - & CH_3 \\ & & \| & & \| & & \\ HO & - & N & & N & - & OH \end{array}$$

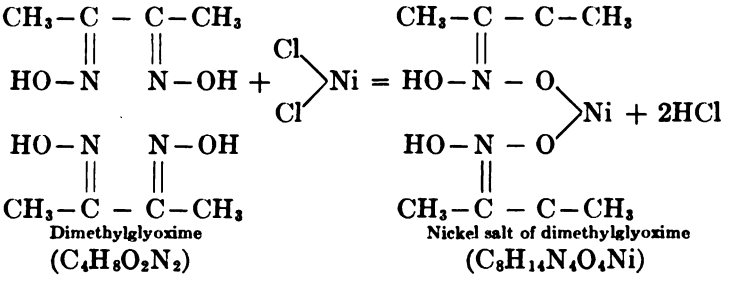
which corresponds to the empirical formula, $C_4H_8O_2N_2$. One

[1] This substance was expensive until a demand arose for it as reagent. In 1908 the price was reduced to about 30 c. a gram but in 1911 it cost only about 4 c. a gram.

[2] *Ber.*, **38**, 2520 (1905).

[3] *Z. angew. chem.*, **20**, 1844 (1907).

atom of nickel replaces 2 atoms of hydrogen in 2 molecules of dimethylglyoxime; the reaction may be written:



The precipitation may be accomplished in the presence of other metals, such as copper, cobalt, chromium, iron, manganese, tungsten and vanadium, provided a sufficient quantity of tartaric acid is present to prevent any precipitation of these elements by means of ammonia. The reagent is not very soluble in water and for this reason care must be taken not to use too large an excess, or the results will be too high.

Requisite Solutions.—*Dimethylglyoxime Solution.*—Dissolve 10 g. of dimethylglyoxime in 1 liter of 98 per cent alcohol and filter if necessary. Ten cubic centimeters of this solution will precipitate approximately 0.025 g. of nickel.

Hydrochloric Acid, approximately 6 normal (*cf.* p. 136).

Procedure.—In a 150-c.c. beaker, dissolve 1 g. of steel in 20 c.c. of 6-normal hydrochloric acid and add about 2 c.c. of concentrated nitric acid to oxidize the iron. Filter the solution and add to the filtrate 6 g. of tartaric acid and water until the volume is about 300 c.c. Add ammonium hydroxide carefully until the solution is slightly ammoniacal. Often a yellow precipitate of basic ferric tartrate is obtained when the solution is neutral but this precipitate will dissolve upon the addition of a little more ammonia. When distinctly ammoniacal there should be no precipitate in the brown solution. If a precipitate is present it indicates too little tartaric acid. Make the solution barely acid with hydrochloric acid, heat it nearly to boiling and add 20 c.c. of the alcoholic solution of dimethylglyoxime, and then ammonia until, after stirring and blowing away the vapors, a faint odor of ammonia can be detected above the solu-

tion. Any nickel present will be precipitated in the form of fine red needles.[1] After allowing the solution to stand a little while, add 10 c.c. more of the dimethylglyoxime solution to see if any further precipitation takes place. If this is the case, it may be necessary to add still more of the reagent.

Allow the solution to stand in a warm place for 1 hr. and then allow to cool for about ½ hr.

Meanwhile prepare a Munroe or Gooch crucible (p. 81), place it in a platinum or nichrome triangle (Fig. 23), heat it at 120° for 1 hr., cool in a desiccator and weigh. Filter the solution through this weighed crucible, using gentle suction. Take care to keep liquid in the crucible and not let the crystals get packed too closely on the asbestos felt, as this interferes with the filtration. Use as gentle suction as will permit rapid filtration. Wash the precipitate with hot water till free from iron (8 to 12 times) and then allow it to drain. Place the crucible in the platinum or nichrome triangle, and heat in a hot closet at 120° for at least ½ hr. Cool in a desiccator and weigh. Heat again in the hot closet to see if the weight is constant.

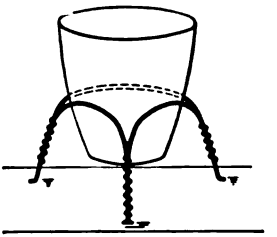


FIG. 23.

To clean the crucible, pick out the greater part of the precipitate without interfering with the asbestos felt, wash with hot dilute hydrochloric acid, then with water and dry at 120°, after which the crucible is ready for use again.

Computation.—If p g. of nickel precipitate were obtained in the analysis of s g. of steel then

$$\text{per cent Ni} = \frac{20.32\,p}{s}$$

NOTES.—1. It is not advisable to attempt to work with too large a nickel precipitate. The weight of sample should be regulated so that the quantity of nickel to be precipitated shall not exceed 0.05 to 0.08 g. Instead of weighing out a very small sample when the alloy is rich in nickel, it is usually better, for the sake of getting a good average sample, to dissolve 2 or 3 g. of the original material and then take an aliquot part for the final precipitation.

[1] If precipitation takes place in the cold, the precipitate is of a slightly different character and filters less readily.

Thus, with a steel containing 25 per cent of nickel, weigh out 3 g. of the material, dilute the solution to 500 c.c. in a calibrated flask, thoroughly mix by pouring back and forth several times into a dry beaker, and then take 50 c.c. (= 0.03 of the sample) for the precipitation with dimethyl-glyoxime.

2. If the nickel content is less than 0.1 per cent, it is not advisable to attempt to carry out the precipitation of the nickel in the presence of all the iron. In such cases, carry out the Rothe ether separation, as described on p. 71 for the separation of iron from manganese, and then proceed as described above using only 2 g. of tartaric acid. Or, in case it is desired to determine other elements in the hydrochloric acid solution, the nickel may be precipitated by hydrogen sulfide in acetic acid solution, the precipitate dissolved in a little aqua regia, the free chlorine boiled off, the solution diluted, and the nickel then precipitated with dimethyl-glyoxime and a slight excess of ammonia.

3. In the analysis of nickel-plated iron and steel, it is often desired to know the depth of the nickel coating. In such cases, dissolve the nickel coating from one or several pieces, the surface area of which has been accurately measured, in cold nitric acid (d. 1.42), pour off the nickel solution into a second beaker, wash the metal several times with strong nitric acid, evaporate off the excess of acid, add tartaric acid and proceed in the usual way to determine the nickel.

Assuming the specific gravity of nickel to be 8.9, the surface of the samples examined to be s sq. mm., and the weight of the nickel precipitate p g., then d, the thickness of the nickel coating, is given by the equation:

$$d = \frac{0.2032\,p}{8.9s}$$

4. *Recovery of Dimethylglyoxime from Nickel Precipitates.*—Triturate the precipitates with a little water in a mortar, rinse the paste into a porcelain evaporating dish and heat, with the addition of a little potassium cyanide, until the nickel salt dissolves forming a reddish-yellow solution. Filter the solution, before letting it stand very long, through a plaited filter to remove asbestos fibers and other insoluble material. Allow the solution to cool and saturate it with pure carbon dioxide gas. At the end of an hour all the dimethylglyoxime will be precipitated. Filter it off on a Büchner suction funnel, wash with cold water, dry and weigh. Dissolve the dry powder in alcohol, using 100 c.c. for each gram of the powder, add a little bone black, heat and filter. The clear solution is now ready for use as reagent.

2. DETERMINATION OF NICKEL BY ELECTROLYTIC DEPOSITION

Principle.—After the removal of the greater part of the iron, preferably by the Rothe ether separation, and the precipitation of the copper as sulfide from acid solution, the nickel may be

deposited electrolytically from an ammoniacal solution containing ammonium sulfate.

Apparatus.—The analysis may be carried out with a platinum spiral as anode and a platinum plate electrode as cathode, but the time required may be shortened by using a cylinder of platinum gauze as cathode, which permits the use of a stronger current. Stirring the electrolyte is also helpful and this can be accomplished very satisfactorily in the Frary apparatus,[1] Fig. 24, which is based upon the principle of the solenoid and causes, by the magnetic influence of the current in the coil of wire in the apparatus, the rotation of the electrolyte while the current is being passed through it. The platinum gauze electrode is required in this apparatus, as it allows the electrolyte to stream through it. The movement of the electrolyte is not satisfactory when a solid electrode is used. In all cases, there is less danger of obtaining spongy deposits with gauze electrodes.

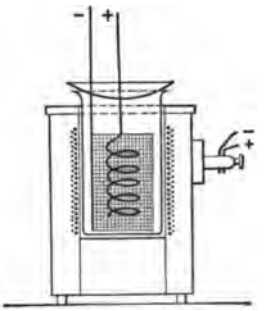


FIG. 24.

Procedure.—Dissolve 3 to 5 g. of an ordinary nickel steel, or 5 to 10 g. of a steel with low-nickel content, in nitric acid, and prepare the solution for the ether separation exactly as described under Manganese, p. 71.[2]

After the removal of the iron by the ether, evaporate the solution to expel the dissolved ether and precipitate the copper as sulfide according to p. 142. Boil the filtrate to expel hydrogen sulfide, add a little sulfuric acid and evaporate until the excess of sulfuric acid is expelled. Treat the residue with sodium hydroxide and sodium peroxide to remove chromium as described under Manganese, p. 76.[3]

After washing out the sodium chromate and other sodium

[1] *Z. Elektrochemie*, **13**, 308 (1907); *J. Am. Chem. Soc.*, **29**, 1592 (1907).

[2] The rapid method described on p. 88 may be used for the removal of the silica.

[3] If chromic salts are present during the electrolysis, they are oxidized to chromate and interfere somewhat with the deposition of nickel. The addition of sodium hypophosphite to the bath before electrolysis is recommended when chromium is present.

compounds, dissolve the oxides (chiefly of nickel, cobalt, manganese and residual iron) by heating with hydrochloric acid (d. 1.10). Dissolve any residue in the platinum dish with a crystal of oxalic acid and a little sulfuric acid, and add the solution to that already obtained. If considerable manganese is present, it is best to neutralize the solution with ammonia, acidify it slightly with acetic acid and precipitate the nickel and cobalt with hydrogen sulfide. Filter off the sulfide precipitate and ignite it in a porcelain crucible. Dissolve it in a little aqua regia and prepare the solution for electrolysis as described below. Small quantities of manganese do no harm and in such cases it is unnecessary to precipitate the nickel and cobalt as sulfides. Add a slight excess of sulfuric acid to the hydrochloric acid solution and evaporate until fumes of sulfuric anhydride are evolved. Add a little water and transfer the solution to a beaker of about 150-c.c. capacity which fits in the Frary apparatus. Add 5 g. of solid ammonium sulfate and 20 to 30 c.c. of strong ammonia in excess of the quantity required to neutralize the solution. Dilute to about 100 c.c., place the beaker in the Frary apparatus and connect the electrodes, as well as the Frary apparatus itself, with the source of electricity. With a current of 5 amperes passing through the solution and a current of about the same strength through the coil, the nickel and cobalt should all be deposited in less than ½ hr. In case the gauze electrode is used with a stationary electrolyte, a current of 0.7 to 1.0 ampere should cause complete deposition in 1 hr. To make sure that the electrolysis is complete, add a little water and note whether any deposition of metal takes place on the freshly exposed electrode surface. If this is not the case, withdraw a few drops of the solution by means of a pipette and add it to a drop of ammonium sulfide on a porcelain spot plate. If no brown precipitate is obtained, the deposition is complete. Disconnect the cathode, quickly withdraw it from the solution and at once transfer it to a beaker containing hot water to free it from adhering ammonium salt. Rinse off the water with alcohol, dry the electrode a short time at 110°, cool and weigh.

The deposited nickel contains any cobalt that may have been present in the sample.

Test Analyses

(*a*) *Pure Nickel Solution.*—Duplicate electrolytic determinations with 50-c.c. portions gave the values 0.1504 g. and 0.1501 g. Ni. Three portions of the same solution were analyzed by the dimethylglyoxime method and the values 0.1502, 0.1505, and 0.1503 g. Ni were obtained.

Two 10-c.c. portions of the same nickel solution (0.0301 g. Ni) were each mixed with 50 c.c. of pure ferric chloride solution (4.8 g. Fe) and to one portion 25 c.c. of manganous chloride solution (0.6 g. Mn) was also added. The nickel was then determined in each solution by adding tartaric acid and dimethylglyoxime with the usual precautions. The values 0.0305 g. and 0.0303 g. Ni were obtained.

(*b*) *Experiments with Nickel Steel.*—Using a sample weighing 0.5 g., the dimethylglyoxime method gave 22.88 per cent Ni, and with 0.2088 g. of the steel the value 23.00 per cent Ni.

Using the electrolytic method and samples weighing respectively 1.000, 3.611, and 3.861 g., the values 23.40, 23.50, and 23.46 per cent Ni were obtained.

The difference between the values obtained by the two methods was due to the fact that the steel contained about 0.51 per cent of cobalt.

(*c*) *Determination of Nickel by the Dimethylglyoxime Method in Various Samples of Commercial Steel.*—Five samples of steel and cast iron with nickel content ranging from 0.01 to 5.05 per cent were analyzed and in all cases duplicates agreed within 0.01 per cent.

Accuracy of the Values and Permissible Deviations

Owing to the fact that the cobalt content of different steels varies considerably, it often happens that the results obtained by the dimethylglyoxime method are considerably lower than those obtained by electrolysis.

If it is desired to know the content of pure nickel, the dimethylglyoxime method is the better method; the electrolytic deposition of the two metals followed by the determination of the cobalt is a much more tedious operation.

The variations in the weights of precipitate in duplicate de-

terminations with dimethyglyoxime should rarely vary more than 1 or 2 mg. When less than 5 per cent of nickel is present, the determinations should agree within 0.02 per cent and within 0.005 per cent if less than 1 per cent of nickel is present.

3. VOLUMETRIC DETERMINATION OF NICKEL BY POTASSIUM CYANIDE[1]

Principle.—When an excess of ammonia is added to a solution containing nickel ions, a pale blue nickel-ammonia complex cation is formed. Thus with nickel chloride the reaction may be written:

$$NiCl_2 + 6NH_3 = [Ni(NH_3)_6]Cl_2$$

This complex nickel-ammonia ion, $Ni(NH_3)_6^{++}$, is fairly stable in solutions containing ammonia, but on adding potassium cyanide a much more stable anion, $Ni(CN)_4^{=}$, is formed

$$[Ni(NH_3)_6]Cl_2 + 4KCN = K_2[Ni(CN)_4] + 6NH_3 + 2KCl$$

The stability of this nickelo-cyanide ion is so great, and its tendency to dissociate into simple nickelous cations and cyanide anions is so slight, that potassium cyanide will not react with insoluble silver iodide until all the nickel-ammonia ions have disappeared. If, then, the solution originally contained some suspended silver iodide, this insoluble compound will react with potassium cyanide, after all the nickel-ammonia ions have disappeared, in accordance with the equation:

$$AgI + 2KCN = K[Ag(CN)_2] + KI$$

The stability of this argenticyanide is also very great. The reason why the potassium cyanide reacts with the nickel-ammonia cations rather than with silver can be traced to the fact that more free nickel ions are present in a slightly ammoniacal solution than there are dissolved silver ions in the liquid which is in contact with precipitated silver iodide.

[1] *cf.* CAMPBELL and ANDREWS, *J. Am. Chem. Soc.*, **17**, 126 (1895); MOORE, *Chem. News*, **72**, 92 (1895); GOUTAL, *Z. angew. Chem.*, **1898**, 177; BREARLEY and JARVIS, *Chem. News*, **78**, 177 and 190; JOHNSON, *J. Am. Chem. Soc.*, **29**, 1201 (1907); CAMPBELL and ARTHUR, *ibid.*, **30**, 1116 (1908); GROSSMANN, *Chem. Ztg.*, **32**, 1223 (1908).

If, after all the nickel and silver have reacted with the potassium cyanide to form complex anions, a little silver nitrate is added, it reacts with the potassium iodide to form a precipitate of silver iodide.

$$KI + AgNO_3 = AgI + KNO_3$$

The volumetric determination of nickel by means of potassium cyanide consists in adding potassium cyanide to a nickel-ammonia solution containing a known quantity of silver iodide until the precipitate dissolves, and then adding just enough more silver to produce a turbidity again. By deducting the volume of potassium cyanide required to react with the silver from the total volume used, the volume of potassium cyanide required to react with the nickel is known.

The method can be carried out in the presence of most of the other elements of the ammonium sulfide group. If copper is present in quantities not exceeding 0.4 per cent, the copper will replace almost exactly three-quarters of its weight of nickel.

When cobalt is present, the solution assumes a dark color upon the addition of potassium cyanide, but if not more than one-tenth of 1 per cent of this element is present in the original sample, the titration can be carried out successfully and the results represent the amount of nickel and cobalt present.

The determination may take place even in the presence of iron if a considerable quantity of citric acid or tartaric acid is first added to the solution. The citric or tartaric acid prevents the precipitation of the iron by ammonia. A dark-colored solution results and the end-point cannot be distinguished readily unless a large excess of the organic acid is added. This will also prevent interference by chromium present as chromic salt.

Necessary Solutions.—*Potassium Cyanide Solution.*—A convenient strength is to make it approximately equivalent to tenth-normal silver nitrate. Since 1 atom of silver reacts with 2 molecules of potassium cyanide, it follows that a tenth-normal solution of potassium cyanide for this analysis should contain one-fifth of a mole dissolved in a liter. To prepare the solution, therefore, dissolve 13.5 g. of pure potassium cyanide in water, add 5 g. of potassium hydroxide dissolved in water, and dilute

the solution to 1 liter. Potassium cyanide containing sulfide cannot be used; it forms a precipitate of silver sulfide with the silver added and silver sulfide is not dissolved by potassium cyanide.

Tenth-normal Silver Nitrate Solution.—Dissolve exactly 8.495 g. of pure silver-nitrate crystals, that have been powdered and dried ½ hr. at 105°, and dilute the solution to exactly 1 liter in a calibrated flask.

Potassium Iodide Solution.—Dissolve 2 g. of potassium iodide in 100 c.c. of water.

To standardize the potassium cyanide solution, measure out about 30 c.c. of it from a burette, dilute to about 100 c.c., add 5 c.c. of potassium iodide solution, and titrate with silver nitrate until a faint permanent opalescence is obtained. The opalescence should be so slight that it can be cleared up by a small drop of potassium cyanide solution. The reactions that take place are as follows:

$$2KCN + AgNO_3 = KAg(CN)_2 + KNO_3$$
$$KI + AgNO_3 = AgI + KNO_3$$

If any AgI is formed before the first reaction is finished it dissolves,

$$AgI + 2KCN = KAg(CN)_2 + KI$$

The end-point is sharper when potassium iodide is present. Without it, a slight excess of $AgNO_3$ would react with the complex cyanide as follows:

$$KAg(CN)_2 + AgNO_3 = KNO_3 + 2AgCN$$

Procedure.—Dissolve 1 g. of steel in a casserole with 10 to 50 c.c. of nitric acid (d. 1.2), adding a little hydrochloric acid if necessary. After the steel has dissolved, add 6 or 8 c.c. of concentrated sulfuric acid, diluted with an equal volume of water, and evaporate until fumes of sulfuric acid are evolved. Cool, add 30 to 40 c.c. of water and boil the contents of the casserole until all the ferric sulfate has dissolved. Transfer the solution to a 400-c.c. beaker, dilute to about 300 c.c. and add 12 g. of powdered citric acid, or, if chromium is present, add twice as much citric acid. When the citric acid has all dissolved make the solution faintly but distinctly alkaline with ammonia.

As the ammonia is added the color of the solution changes. The solution turns green, then yellow, and finally assumes a brownish shade when the ammonia is present in excess. With the large amount of citric acid used, the color is not such a deep red as when only a little is present.

To the cold solution, which is alkaline to litmus but does not contain a large excess of ammonia, add about 2 c.c. of the potassium iodide solution and enough of the tenth-normal silver nitrate from a burette to produce a distinct turbidity. About 0.5 c.c. of silver nitrate is sufficient. The solution is now ready for titration with potassium cyanide.

Add the potassium cyanide solution, while stirring constantly, until the precipitate of silver iodide disappears. Then finish the titration by adding just enough silver nitrate to cause the formation of a very slight turbidity.

Computation.—If 1 c.c. of potassium cyanide solution is equivalent to t c.c. of tenth-normal silver nitrate solution, and n_1 c.c. of silver nitrate together with n_2 c.c. of potassium cyanide are used in the analysis of a sample of steel weighing s g., then

$$\text{per cent Ni} = \frac{(n_2 t - n_1)\, 0.2934}{s}$$

NOTE.—The temperature of the solution should not be much above 20° during the titration. Too large an excess of ammonia should not be present as it tends to impede the course of the reaction by making the nickel-ammonia complex more stable so that it is not decomposed readily by the potassium cyanide.

The method is often used after the removal of the iron by the ether method. It is then easier to carry out the titration. The results are accurate.

4. DETERMINATION OF NICKEL BY THE VOLUMETRIC-DIMETHYLGLYOXIME METHOD[1]

Principle.—The nickel is precipitated as the salt of dimethylglyoxime and the precipitate dissolved in nitric acid. The organic matter is oxidized by treatment with ammonium persulfate and the nickel determined by potassium cyanide titration. The method is recommended for routine work.

[1] *Am. Soc. Testing Materials*, **1915**, 221.

Solutions Required—*Hydrochloric Acid, approximately* 6-*normal.*—(See p. 136.)

Dimethylglyoxime.—(See p. 176.)

Silver Nitrate.—Dissolve 0.5 g. of silver nitrate in 1,000 c.c. of distilled water.

Potassium Iodide.—Dissolve 20 g. of the solid in 1,000 c.c. of distilled water.

Standard Potassium Cyanide.—Dissolve 2.3 g. of the salt in 1,000 c.c. of water. To standardize the potassium cyanide solution, first titrate about 30 c.c. of it (accurately measured) and 5 or 10 c.c. of potassium iodide solution (approximately) with silver nitrate solution till a faint permanent opalescence is obtained. Then standardize the solution against a steel of known nickel content, *e.g.* Bureau of Standards Steel No. 33, using the method to be described. In every titration a deduction must be made for the potassium cyanide equivalent to the silver nitrate added. For convenience it is well to adjust the concentration of the potassium cyanide solution so that 1 c.c. = 0.0005 g. Ni = 0.05 per cent in the analysis of a 1-g. sample.

Procedure.—Proceed exactly as in Method 1 till the precipitate of dimethylglyoxime salt is obtained on the Gooch filter. Dissolve the precipitate by the addition of 10 to 20 c.c. of hot concentrated nitric acid, added drop by drop, and wash the filter five times using suction. To the solution in a 500-c.c. beaker, add 3 g. of ammonium persulfate and boil for 5 min. Cool, make distinctly ammoniacal, add exactly 10 c.c. of silver nitrate (from a burette or pipette) and about 10 c.c. of potassium iodide solution from a graduate. Titrate with potassium cyanide to a faint turbidity.

5. DETERMINATION OF NICKEL BY POTASSIUM CYANIDE TITRATION AFTER ETHER EXTRACTION

Principle.—The greater part of the iron is removed by the Rothe Method (p. 71) and the remainder by precipitation with ammonium hydroxide, the copper is removed by precipitation as sulfide from the acid solution and the nickel determined in the filtrate by potassium cyanide titration.

Solutions Required—*Hydrochloric Acid.*—Mix 600 c.c. of concentrated acid, d., 1.2 with 400 c.c. of water.

Nitric Acid.—Mix 1,000 c.c. of concentrated acid, d. 1.42 with 1,200 c.c. of distilled water.

Potassium Iodide, Silver Nitrate and *Standard Potassium Cyanide* solutions as in the preceding method.

Procedure.—In a 150-c.c. beaker, dissolve 1 g. of the steel in 20 c.c. of the hydrochloric acid and oxidize the iron by 2 c.c. of the nitric acid, boiling until all oxides of nitrogen are expelled. Cool and transfer the solution to a 250-c.c. separatory funnel rinsing out the beaker with small portions of the acid. Add 50 c.c. of ether, shake for 5 min., let stand for 1 min. and then draw off the lower layer of solution into another separatory funnel. Add 10 c.c. of concentrated hydrochloric acid to the ethereal solution of ferric chloride in the first funnel, cool, shake and withdraw the lower liquid into the second funnel. Then discard the ether in the first funnel, or preserve it to recover the ether by distillation from a water-bath away from any flame.

Shake the solution in the second separatory funnel with another 50-c.c. portion of ether and withdraw the solution into a 150-c.c. beaker, rinsing the ether, as before, with a little strong hydrochloric acid.

Heat the solution carefully on the water bath to expel the ether, add 0.2 g. of potassium chlorate, boil until the chlorate is decomposed, dilute to 100 c.c. with hot water, make faintly ammoniacal and boil for 5 min. Filter and wash with hot water. Rinse the ferric hydroxide precipitate back into the original beaker, pour a little hydrochloric acid through the filter to dissolve the adhering precipitate and again precipitate with ammonium hydroxide of which a little is also poured through the filter. Filter off the ferric hydroxide and wash with hot water at least six times.

To the combined filtrates add 10 c.c. of concentrated hydrochloric acid and precipitate the copper with hydrogen sulfide. Filter and wash with hot water. Boil the filtrate to expel hydrogen sulfide and concentrate the solution to about 100 c.c. Cool, make distinctly ammoniacal, add 10 c.c. each of standard silver nitrate and potassium iodide solutions and titrate with standard potassium cyanide to a clear solution.

CHAPTER XI

MOLYBDENUM

Molybdenum is seldom present as impurity in iron or steel but is sometimes added intentionally. Ferro-molybdenum, chrome-molybdenum and metallic molybdenum are used in the preparation of special steels.

Molybdenum is interesting to the chemist because it has so many typical reactions. Compounds representing at least five different states of oxidation are known, corresponding to the oxides MoO, Mo_2O_3, MoO_2, MoO_3 and Mo_2O_7. The first three oxides have basic properties and the last two are acid anhydrides. The analytical chemist often refers to other oxides, such as $Mo_{12}O_{19}$ or $Mo_{34}O_{37}$, but it is probable that these represent merely a partial oxidation of trivalent molybdenum to the quadrivalent or hexavalent state. Following the old dualistic nomenclature, according to which a salt was regarded as an oxide of a metal combined with an oxide of a non-metal (*e.g.* K_2SO_4 was $K_2O{\cdot}SO_3$ and Na_2CO_3 was $Na_2O{\cdot}CO_2$) it is a common, though deplorable, practice for analytical chemists to call the oxide MoO_3 molybdic acid and to speak of the oxidation of molybdic sulfate to molybdic acid as the oxidation of Mo_2O_3 to MoO_3. To make this point clear, let us compare typical oxidation and reduction reactions of molybdenum with those of iron.

According to the dualistic nomenclature the reduction of ferric salt in acid solution by means of zinc is expressed as follows:

$$Zn + Fe_2O_3 = ZnO + 2FeO$$

and the oxidation back to ferric salt by means of permanganate is written

$$10FeO + Mn_2O_7 = 5Fe_2O_3 + 2MnO$$

Now we know that there is absolutely no evidence of any free ZnO, FeO or Fe_2O_3 being formed at any time; in fact these oxides cannot form because an excess of free acid is present in the analy-

tical process. The modern, and somewhat simpler way to write these reactions is as follows:

$$Zn + 2Fe^{+++} \rightarrow 2Fe^{++} + Zn^{++}$$
$$5Fe^{++} + MnO_4^- + 8H^+ \rightarrow 5Fe^{+++} + Mn^{++} + 4H_2O$$

In exactly the same way, the oxidation and reduction of molybdenum compounds is usually written

$$3Zn + 2MoO_3 = 3ZnO + Mo_2O_3$$
$$5Mo_2O_3 + 3Mn_2O_7 = 6MnO + 10MoO_3$$

but these equations are preferable written like this:

$$3Zn + 2H_2MoO_4 + 12H^+ \rightarrow 3Zn^{++} + 2Mo^{+++} + 8H_2O$$
$$5Mo^{+++} + 3MnO_4^- + 3H_2O \rightarrow 5H_2MoO_4 + 3Mn^{++} + 6H^+$$

The best known compounds of molybdenum are molybdic acid anhydride, MoO_3, ammonium molybdate, $(NH_4)_2MoO_4$ (the commercial salt corresponds to the symbol $3(NH_4)_2MoO_4{\cdot}4H_2MoO_4$) and ammonium phosphomolybdate, $(NH_4)_3PO_4{\cdot}12MoO_3$.

In qualitative schemes of analysis, molybdenum is usually classed with arsenic, antimony and tin because the brown sulfide, MoS_3, is precipitated by means of hydrogen sulfide or by saturating an ammonium molybdate solution with hydrogen sulfide, forming $(NH_4)_2MoS_4$) and then adding acid:

$$MoS_4^= + 2H^+ \rightarrow MoS_3 + H_2S \uparrow$$

Molybdic acid anhydride is very slightly soluble in water but solutions of mineral acids dissolve it appreciably. When much molybdenum is present, however, a little of the acid is precipitated with the silica upon evaporating the acid solution to dryness. By fusion with alkaline fluxes, molybdenum compounds are converted into water-soluble alkali molybdate, and by fusion with sodium carbonate and sulfur, sodium thiomolybdate, Na_2MoS_4, is formed which is soluble in water; on adding acid to the aqueous solution of sodium thiomolybdate, molybdenum sulfide is precipitated.

In several methods that have been described for the analysis of iron and steel, ferric chloride has been dissolved out of the hydrochloric acid solution by shaking with ether; molybdenum follows the iron in this treatment.

One of the most sensitive tests for molybdenum is based upon the fact that when a little molybdenum compound is heated with a drop of sulfuric acid on porcelain until nearly all the sulfuric acid has been driven off, the cooled mass will be an intense blue (breathing upon it sometimes brings out the color but water destroys it). This test can be obtained with less than 0.1 mg. of molybdenum oxide, but it is not always obtained with an impure product.

From neutral solutions of alkali molybdate, mercurous nitrate precipitates white mercurous molybdate and lead acetate precipitates white lead molybdate; both these precipitates are easily dissolved by nitric acid. Potassium ferrocyanide produces a brown precipitate or, in the presence of oxalic acetic or phosphoric acids, a brown coloration. Sodium phosphate added to a nitric acid solution of a molybdate gives a yellow precipitate of ammonium phosphomolybdate. Potassium thiocyanate, KCNS, causes no reaction with molybdenum when added to a molybdic acid solution containing hydrochloric acid but if the acid solution is then treated with zinc or stannous chloride, a blood-red coloration is obtained, similar to that obtained with ferric ions and potassium thiocyanate; this is also a sensitive test for molybdenum. If a dry molybdenum compound is dissolved in concentrated ammonium hydroxide and then hydrogen peroxide is added, the solution is at once turned pink or red; on evaporating to dryness and treating the residue with sulfuric or nitric acid, yellow permolybdic acid, $HMoO_4$, is obtained.

Zinc, aluminium, stannous chloride and other reducing agents added to an acid solution of molybdate causes a reduction of the molybdenum; the solution is colored blue, then green and finally brown. Sulfurous acid will not give the reaction in strongly acid solution.

1. DETERMINATION OF MOLYBDENUM BY THE SODIUM PEROXIDE FUSION METHOD

Principle.—The molybdenum is converted into water-soluble sodium molybdate by fusion with sodium peroxide in a nickel or iron crucible. In the aqueous extract of the melt, the sodium molybdate is converted into sodium thiomolybdate and the latter into molybdenum sulfide, MoS_3, by adding acid.

Procedure.—If the material can be pulverized, fuse 1 to 2 g. of the powder with 6 times as much of Rothe magnesia-sodium carbonate mixture (1:2), at not too high a temperature, and extract the ignited product with hot water (p. 125). Of steel filings or drillings, dissolve 2 to 3 g. in nitric acid (d. 1.2), destroy the nitrates as described on page 165, and fuse the oxides with sodium peroxide in a nickel crucible at a relatively low temperature.

After extracting with water, filter off the undissolved oxides, wash well and fuse again with 3 to 6 g. pure sodium carbonate in a platinum crucible. Extract the product of this fusion with water and add the filtered solution to that previously obtained.

The filtrates now contain beside all the molybdenum, any vanadium, tungsten, phosphorus, silicon, etc., that was originally present. If the molybdenum content is considerable, dilute up to the mark in a calibrated flask and use an aliquot part of the well-mixed solution for the further analysis. If the molybdenum content is small, use the entire solution.

Neutralize the greater part of the alkali with dilute sulfuric acid, evaporate the solution to 50 to 100 c.c., add 25 c.c. of strong ammonia, and saturate the solution with ammonium sulfide. Then acidify with dilute sulfuric acid and warm the solution while passing hydrogen sulfide gas through it. In this way there is no difficulty in precipitating all the molybdenum as sulfide.

If tungsten is present, add tartaric acid to the solution before making it acid. This prevents the precipitation of tungsten.[1]

Filter off the precipitate of molybdenum sulfide and wash the precipitate with very dilute sulfuric acid and finally with water. Ignite the precipitate with the filter in a weighed porcelain crucible at as low a temperature as possible.[2]

Heat the crucible at first with a very low flame so that the point of the flame just touches the crucible, placing this flame at the front of the crucible until all the moisture is expelled and then at the base of the crucible, so that escaping hydrocarbons will not take fire. Turn the crucible a little from time to time to hasten the decomposition into molybdenum oxide, MoO_3. Finally, when all but a little of the carbon has been consumed,

[1] FRIEDHEIM and MEYER, *Z. anorg. Chem.*, **1**, 76 (1892).

[2] *Cf.* FRIEDHEIM and EULER, *Ber.*, **28**, 2061 (1895).

dissolve the oxide in a little ammonia, add a few crystals of ammonium nitrate, evaporate carefully to dryness, and ignite until all the ammonium salts are volatilized. If necessary, repeat this treatment till all the carbon is consumed.

If vanadium is present, the molybdenum trioxide has a dark color. After weighing the oxides, dissolve them in a little caustic soda solution and determine the vanadium by Method 2 or 3. pp. 210, 212. Deduct the corresponding amount of vanadium pentoxide (1 c.c. normal solution = 0.0091 g. V_2O_5) from the weight of impure molybdenum oxide.

If arsenic is present, it may be removed by precipitating the ammoniacal solution with magnesia mixture before precipitating the molybdenum; the arsenic is precipitated as magnesium ammonium arsenate, which on ignition is changed to magnesium pyroarsenate, $Mg_2As_2O_7$.

The filtrate from the hydrogen sulfide precipitation will have a violet or bluish-green color if chromium and vanadium are present. It may be tested again with hydrogen sulfide to see if the precipitation of the molybdenum sulfide was complete.

Pure molybdenum oxide has a light yellow color when cold. On adding a drop of sulfuric acid and evaporating off the excess acid, a beautiful blue color is obtained.

Computation.—If p g. of pure molybdenum trioxide were obtained from s g. of steel, then

$$\text{per cent Mo} = \frac{66.67 \times p}{s}$$

2. DETERMINATION OF MOLYBDENUM BY THE ETHER EXTRACTION METHOD OF BLAIR[1]

Principle.—The molybdenum is precipitated in acid solution by hydrogen sulfide under pressure and the molybdenum sulfide thus obtained is converted into molybdenum trioxide, MoO_3, which is weighed.

Procedure.—Carry out the solution of the sample and treatment with ether exactly as described under Manganese. The molybdenum will be found in the etherial solution which was discarded in the manganese determination. (See also Sulfur.)

[1] *J. Am. Chem. Soc.*, **30**, 1228.

Evaporate the ether solution nearly to dryness, add 10 c.c. of concentrated sulfuric acid and again evaporate to remove the hydrochloric acid. Cool, dissolve in about 100 c.c. of water and reduce the ferric salt by adding ammonium bisulfite. Boil off the excess of sulfurous acid and cool the solution. Transfer it to a 200-c.c. pressure bottle, saturate with hydrogen sulfide gas, stopper the bottle, and heat on the water bath for several hours. Allow the solution to cool slowly, open the bottle, and filter off the molybdenum sulfide. Ignite it as described above and weigh the pure molybdenum oxide, MoO_3.

3. VOLUMETRIC DETERMINATION OF MOLYBDENUM

Principle.—The sample is dissolved in mineral acids and the iron separated from the molybdenum by pouring the nearly neutral solution into an excess of sodium hydroxide solution. The ferric hydroxide is filtered off and an aliquot part of the filtrate is saturated with hydrogen sulfide; any resulting precipitate is filtered off and the molybdenum is precipitated as sulfide by adding acid to the alkaline sulfide solution. The molybdenum sulfide is dissolved in acid, reduced to the trivalent condition by means of zinc, oxidized back to the hexavalent condition by ferric sulfate solution and the reduced iron determined by titration with permanganate (*cf.* Phosphorus, Method 6).

Procedure.—Dissolve 2 g. of drillings in a porcelain casserole with 25 c.c. of concentrated hydrochloric acid and add about 2 c.c. of concentrated nitric acid to oxidize the iron to the ferric state.

If a precipitate of tungstic acid appears, filter it off, fuse with a little sodium peroxide in a nickel or iron crucible and examine for molybdenum as in Method 1. If a precipitate of molybdenum sulfide is obtained, ignite and weigh it as oxide. Compute the per cent of molybdenum thus obtained and add it to that obtained in the main analysis, remembering that the sample weighed 2 g. whereas but 1 g. is used in the volumetric determination.

Nearly neutralize the acid solution of the steel with 2-normal sodium hydroxide and heat to the boiling point. Pour the hot solution very slowly through a narrow-stem funnel into 70 c.c. of 2-normal sodium hydroxide solution contained in a 500-c.c.

calibrated flask. Cool, make up to the mark with water and mix thoroughly. Allow the precipitate to settle and filter through a dry filter until half the solution has been collected in a 250-c.c. calibrated flask. Nearly neutralize the filtrate with dilute sulfuric acid, concentrate to about 100 c.c., add 25 c.c of concentrated ammonium hydroxide (d. 0.90), and saturate the cold solution with hydrogen sulfide. If a precipitate appears, filter it off and wash the filter with hot water. If tungsten is likely to be present, add 2 g. of tartaric acid and then add sulfuric acid to acid reaction. Heat the solution, while passing hydrogen sulfide into it, and filter hot. Wash the precipitate of MoS_3 with very dilute sulfuric acid which has been saturated with hydrogen sulfide.

Dissolve the precipitated molybdenum sulfide in hot, 6-normal nitric acid catching the solution in a porcelain casserole. Add 10 c.c. of concentrated sulfuric acid and evaporate till fumes of sulfuric acid are evolved. Cool, wash down the sides of the dish with water and again evaporate till dense fumes are evolved. This second evaporation is to make sure that every trace of nitric acid is removed; if left in solution it will be reduced in the subsequent precedure and cause the results to come out too high.

Finally dilute to about 100 c.c. and boil with granulated zinc to remove any copper. Filter through an alundum or asbestos filter and then run through a Jones reductor as described on page 108 allowing the reduced solution to run into ferric alum and titrating the reduced iron.

Computation.—In this process the molybdenum changes from the trivalent to the hexavalent condition in the final oxidation by ferric salt and an equivalent quantity of iron is reduced. 1 c.c. of normal permanganate $= \frac{Mo}{3{,}000} = 0.0320$ g. of molybdenum. Or, if the solution of permanganate has been standardized against sodium oxalate, the molybdenum value of 1 c.c. is obtained by multiplying the sodium oxalate value by $\frac{2Mo}{3Na_2C_2O_4} = 0.4776$. According to the above directions, only one-half the original weight is used in the final analysis.

CHAPTER XII

TUNGSTEN

Tungsten is not found very often in steels. It is never present as impurity but is intentionally added in special alloy steels such as high-speed steels in quantities up to 20 per cent or even more.

When treated with an oxidizing acid, metallic tungsten is converted into tungstic acid, or its anhydride, WO_3. All of the important tungsten minerals are salts of this acid. The trioxide is a canary-yellow powder, insoluble in water and in dilute acids but readily dissolved by boiling with caustic alkali solutions and less readily by ammonium hydroxide. In quantitative analysis tungstic acid is precipitated in much the same way that silicic acid is obtained or, from a nearly neutral solution of an alkali tungstate, precipitates of mercurous or lead tungstates may be obtained, both of which are white. Mercurous and ammonium tungstates are decomposed by gentle ignition and tungstic acid anhydride, WO_3, is left behind. This is itself volatile upon strong ignition.

Reducing agents such as zinc and hydrochloric acid and stannous chloride give characteristic reactions with a dilute solution of alkali tungstate. The final reduction products are blue in color, probably due to the formation of WCl_5.

By boiling with dilute hydrochloric acid, all tungsten can be precipitated as the trioxide provided no colloidal solution is formed. Alkali salts, however, render the complete deposition of tungsten trioxide difficult. The precipitation of tungstic acid anhydride can be hastened and the interfering effects of certain dissolved salts lessened by means of a solution of cinchonine hydrochloride.

1. DETERMINATION OF TUNGSTEN AS TRIOXIDE BY PRECIPITATION FROM AN ACID SOLUTION CONTAINING CINCHONINE HYDROCHLORIDE[1]

Principle.—The tungsten in the steel is oxidized to tungstic acid by treatment with concentrated nitric and hydrochloric

[1] C. M. JOHNSON (*Rapid Methods for the Chemical Analysis of Special Steels*) has recommended the use of cinchonine hydrochloride solution to

acids and the precipitation of the tungstic acid is rendered complete by the addition of cinchonine hydrochloride. After filtering off the precipitate it is purified by dissolving it in ammonium hydroxide and reprecipitating it by the addition of acid. The precipitate is ignited at a low temperature, to avoid volatilization of the tungsten, and weighed as tungsten trioxide, WO_3.

Solutions Required.—*Concentrated Nitric Acid* (d. 1.42); *Concentrated Hydrochloric Acid* (d. 1.2); and *Concentrated Ammonium Hydroxide* (d. 0.90).

Cinchonine Hydrochloride.—Dissolve 125 g. of cinchonine in 500 c.c. of concentrated hydrochloric acid and dilute with an equal volume of water.

Cinchonine Wash.—Use 10 c.c. of cinchonine hydrochloride solution to 1 liter of hot water.

Ammonia Wash.—To 800 c.c. of water add 200 c.c. of concentrated ammonium hydroxide and 10 c.c. of concentrated ammonium chloride.

Filter-paper Pulp.—Macerate small pieces of ashless filter paper with hot water.

Procedure.—Weigh 2 g. of steel into a 400-c.c. beaker, cover with a watch-glass and add 60 c.c. of a mixture of equal parts concentrated nitric and hydrochloric acids. When the steel is all dissolved, add 40 c.c. of concentrated hydrochloric acid and 20 c.c. of concentrated nitric acid and evaporate the solution to a volume of 10 or 15 c.c. Stir the residue when adding the fresh acid and break up any crust that may form during the evaporation.

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hasten the precipitation of tungstic acid from acid solutions. The method given here was recommended by J. A. Holliday (chemist for the Electro Metallurgical Company of Niagara Falls) for the analysis of tungsten ores. The method has been tested out at the Bureau of Standards and by a number of other chemists and it has been found to give accurate results. M. C. Hawes, working as a student at the Massachusetts Institute of Technology, found that there was danger of losing tungstic anhydride by volatilization unless care was taken in the final ignition not to expose the contents of the crucible to the full heat of the burner; the crucible should not be covered. D. Belcher, in 1916, also found it easy to volatilize tungstic anhydride although it has been stated repeatedly that the full heat of a Bunsen burner can be used.

If, by accident, the contents of the beaker should go to dryness, add 50 c.c. of hydrochloric acid and again reduce to small volume.

Dilute the solution with 150 c.c. of hot water, add 5 c.c. of cinchonine hydrochloride solution and digest on the hot plate, at a temperature near the boiling point, for 30 min. Allow the precipitate to settle and decant off the solution through an ashless paper filter containing filter-paper pulp. Wash the tungstic acid residue three times by decantation with hot "cinchonine wash" solution. Transfer the precipitate to the filter and continue washing until the ferric chloride is all removed.

Rinse the precipitate back into the original beaker using not more than 25 c.c. of water. Add 6 c.c. of concentrated ammonium hydroxide and gently heat the contents of the covered beaker for about 10 min. Wash down the sides of the beaker with warm "ammonia wash" solution, stir, and filter through the original filter. Wash the filter thoroughly with the "ammonia wash" solution until all the tungsten is in the filtrate in the form of ammonium tungstate.

Evaporate the ammoniacal solution until all the free ammonia has been expelled. This point is important because an excess of ammonium salt will render the subsequent precipitation of the tungsten incomplete. Then add 20 c.c. of concentrated hydrochloric acid and 10 c.c. of concentrated nitric acid and digest at 80 to 90° for about 30 min. Add an excess of filter-paper pulp and filter through a 9-cm. filter paper. Wash thoroughly with hot "cinchonine wash solution."

Ignite in a platinum crucible at a low-red heat until all the carbon has been oxidized and then for not more than 1 min. longer. The full heat of a Tirrill burner will cause volatilization of tungstic acid.

The presence of the paper pulp causes the precipitate to dry to a porous, friable mass from which the carbon is easily removed by ignition at a low temperature. The ignited oxide contains 79.31 per cent of tungsten.

2. DETERMINATION OF TUNGSTEN BY THE DEISS METHOD

Principle.—On treating a steel containing tungsten with an oxidizing acid solvent, all the tungsten is converted into tungstic acid anhydride, WO_3. The precipitation of this substance may

be made quantitative from hydrochloric acid solutions provided precautions are taken to prevent some of it remaining in the colloidal condition as hydrosole.

Procedure.—If the material is low in tungsten use a 10-g. sample, otherwise use 5 g. or less. Weigh the sample into a porcelain casserole and dissolve it in dilute nitric acid (d. 1.2) using 110 c.c. for a 10-g. portion and 60 c.c. for a 5-g. portion. The material should be in the form of fine turnings. Steels with much tungsten often resist the action of nitric acid, but in most cases they may be dissolved slowly by adding a few drops of concentrated hydrochloric acid, waiting till all action has ceased, and repeating the addition of hydrochloric acid from time to time.

Evaporate the solution to dryness and heat the residue to decompose the nitrates. When no more nitrous fumes are evolved by strongly heating the residue, cool it somewhat, moisten with concentrated hydrochloric acid (d. 1.2) and heat gently with 50 c.c. of hydrochloric acid (d. 1.12) until finally all the ferric oxide has dissolved. The residue of silica and tungstic acid anhydride should not be colored red with ferric oxide after this treatment with hydrochloric acid. Again evaporate the solution to dryness on the water bath and heat the residue at 135° till no more acid vapors are evolved. Then moisten the residue once more with concentrated hydrochloric acid and dissolve all the iron by heating with 6-normal hydrochloric acid, but do not continue heating after all the basic ferric chloride has dissolved. Evaporate off the excess of hydrochloric acid, continuing the process as far as possible without causing solid to separate out; in this way a thick sirup is obtained. It is necessary to follow these directions carefully in order to make the precipitation of the tungsten quantitative.

Allow the thick sirup to cool and then dilute with an equal volume of dilute hydrochloric acid (1 part conc. acid to 5 parts water), stir and allow to stand a few minutes. Filter off the deposited silica and tungsten trioxide through an ashless filter. Rinse the precipitate from the dish to the filter by means of dilute hydrochloric acid from a wash bottle. Usually, when tungsten is present, a yellow film of tungsten trioxide remains adhering to the porcelain dish. After washing the dish and filter with dilute hydrochloric acid till free from iron, rub the dish with a

filter paper moistened with ammonia water and add the paper to the contents of the filter; the ammonia dissolves the yellow tungsten trioxide forming ammonium tungstate which is converted back to the oxide upon ignition. Finally rub the dish with a piece of filter paper moistened with alcohol.

If the tungsten content is high the residue often filters badly. It is a good plan in such cases to add, before filtering, a little filter paper pulp prepared by shaking small pieces of filter paper with hot water; this prevents the pores of the filter from becoming immediately clogged with fine precipitate. Traces of tungsten trioxide may pass through the filter and sometimes the turbidity thus produced is scarcely noticeable. In all cases, therefore, evaporate the filtrate in a 250-c.c. beaker as far as possible without causing solid salts to deposit and allow the liquid to cool. Then, if any tungsten trioxide has passed through the filter, it will settle out on the bottom of the beaker and be distinctly visible. To recover such a precipitate, dilute as before and filter through a fresh filter.

The filtrate may now be used for the determination of other elements such as manganese, nickel, chromium, phosphorus, etc.

Heat the filters and precipitates at a low temperature till all the carbon is consumed and finally ignite to a constant weight over the full heat of the Bunsen or Tirrill burner. The crucible must not be heated over the blast lamp because at high temperatures tungstic acid is volatilized slowly.

After weighing the precipitate of silica and tungsten trioxide, moisten it with about 5 drops of sulfuric acid (1 : 1) and add about 2 c.c. of hydrofluoric acid. Evaporate as far as possible on the water bath, or preferably in an air bath, and then heat very carefully with the free flame until the sulfuric acid is expelled. Finally heat strongly with the same burner that was used for heating the impure tungsten trioxide. The loss in weight corresponds to the amount of silica, SiO_2, present and from this the quantity of silicon in the steel can be computed. The residue in the crucible, however, cannot be regarded as pure tungsten trioxide. It is invariably contaminated with a little ferric oxide and may contain some mangano-manganic oxide, Mn_3O_4, chromic oxide, Cr_2O_3, titanium dioxide, TiO_2, and possibly traces of vanadium pentoxide, V_2O_5, or molybdenum trioxide, MoO_3. To

purify the precipitate, fuse it with about six times as much sodium carbonate. Extract the fused mass with a little water, wash the crucible and its cover carefully, and filter off the insoluble residue upon a small filter. Wash the precipitate thoroughly with hot water and then ignite it in the same crucible, without attempting to clean it after washing out the soluble sodium salts. The residue contains all the iron and titanium that contaminated the tungsten trioxide; in most cases the weight of this residue subtracted from the previous weight of impure tungsten trioxide obtained after the removal of the silica will give the weight of pure tungsten trioxide. For the direct determination of the tungsten, the sodium tungstate solution, which may be contaminated with chromium as shown by a yellow colored solution, is treated with mercurous nitrate solution in the following manner.

Add a piece of litmus paper to the solution in a 300 to 400-c.c. beaker, cover the beaker with a watch glass to prevent loss by effervescence, and carefully neutralize the solution with dilute nitric acid (1 part concentrated acid to 5 parts of water). Expel all the carbonic acid from the solution by boiling gently and then add to the hot, neutralized solution some mercurous nitrate reagent (p. 159) until no further precipitation is produced. Stir the solution and continue the boiling for a short time. Allow the precipitate to settle and test with a little more mercurous nitrate to see if the precipitation was complete. Again heat to boiling, allow the precipitate to settle and add 2 or 3 drops (not more) of 6-normal ammonia (d. 0.96). This addition of ammonia serves to neutralize the acid of the mercurous nitrate solution (*cf.* p. 163). If the ammonia is not added some of the tungsten may remain dissolved as metatungstate. On the other hand, if too much ammonia is added, this will cause some of the precipitate to dissolve. Many chemists, therefore, prefer not to use ammonia and add instead a paste containing precipitated mercuric oxide stirred up with water. Then, by heating the solution with this paste, the excess of acid can be neutralized.

The addition of the few drops of ammonia should cause the formation of a black precipitate, $Hg\begin{matrix}NH_2\\NO_3\end{matrix}$ + Hg, showing that

an excess of mercurous ions is present in the solution. Stir the solution well and boil for a short time. The precipitate should retain its gray color during the boiling; if it becomes yellow again it is necessary to add a little more ammonia and treat as before.

Allow the precipitate to settle and then decant the clear solution through an ashless filter. When all the clear solution has been poured through the filter, cover the precipitate with hot water and add a few c.c. of mercurous nitrate solution. Boil a short time and again decant the solution through the filter. Continue this treatment once or twice more in order to remove all the soluble alkali salts. Then transfer the precipitate to the filter and wash a few times with hot water.

The precipitate adhering to the sides of the beaker can usually be removed by rubbing it with a moist piece of filter paper; in case it has dried to the sides of the beaker and is hard to remove, use a filter moistened with a little nitric acid. Place the filter paper used for wiping out the beaker in a weighed platinum crucible and burn this paper by itself, allowing the air to enter the crucible freely. Then add the main precipitate while still moist on the filter and ignite carefully under a good hood. This ignition may take place without danger in a platinum crucible provided plenty of air is allowed to enter the crucible.

After the filter paper is all consumed, ignite the contents of the crucible to constant weight over a Bunsen burner.

If the solution is colorless before the addition of the mercurous nitrate solution, there is no chromium present and the contents of the crucible usually consists of practically pure tungsten trioxide of light yellow color. A green coloration may be caused by the presence of a little alkali or of a trace of molybdenum trioxide.

If the solution was yellow before the addition of the mercurous nitrate solution, chromium is present and the ignited tungsten trioxide contains chromium and has a greenish-gray color.

As the tungsten was originally precipitated from strongly acid solution, it seldom happens that much chromium is present at this stage of the analysis. After weighing the impure tungsten trioxide, the chromium may be determined by fusing the residue with sodium carbonate, dissolving the melt in water, acidifying

with hydrochloric acid and treating with potassium iodide and sodium thiosulfate solution (p. 161) or the residue in the crucible may be fused with the potassium acid tartrate mixture (p. 164) and the sodium tungstate, now free from chromium, washed out with water. The weight of chromic oxide, Cr_2O_3, obtained by computation from the volume of sodium thiosulfate used, or by direct weighing of the residue after the potassium acid tartrate fusion, deducted from the weight of impure tungsten trioxide, gives the weight of the pure substance. The uncolored filtrate from the potassium acid tartrate fusion may be used for the direct precipitation of the tungsten or, in special cases, for the determination of vanadium and molybdenum.

Computation.—If p represents the weight of pure tungsten trioxide obtained in the analysis of s g. of material then

$$\text{per cent W} = \frac{p}{s} 79.31$$

3. DETERMINATION OF TUNGSTEN BY THE SODIUM-PEROXIDE-FUSION METHOD[1]

Principle.—If a mixture of ferric oxide and tungstic acid anhydride is fused with sodium peroxide, the latter is converted into soluble sodium tungstate and may be separated from the ferric oxide by extracting the melt with water. The tungsten may be precipitated by means of mercurous nitrate but the mercurous tungstate will be contaminated by mercurous phosphate, chromate, vanadate and molybdate to the extent that phosphorus, chromium, vanadium and molybdenum are present in the original material; a little silica is also likely to be carried down. The precipitate, therefore, must undergo further treatment in order to obtain pure tungsten trioxide.

Procedure.—Weigh out 2 g. of tungsten steel containing about 5 per cent tungsten, or 1 g. of a steel richer in tungsten, into a small porcelain casserole. Cover the casserole with a watch-glass and treat the steel with 30 c.c. of nitric acid (d. 1.2). When the steel is dissolved, evaporate the solution to dryness and heat the residue, keeping the dish covered with a watch-glass, until

[1] HINRICHSEN, *Mitt. Kgl. Materialprüfungsamt*, **25**, 308 (1907) or *Stahl u. Eisen*, **27**, 1418 (1907).

no more nitrous fumes are evolved. The oxides then become detached, for the most part, from the sides of the dish.

Transfer the oxides as completely as possible to an agate mortar and mix them with six or eight times as much pure sodium peroxide. Add the mixture to a nickel crucible. Sprinkle a little more sodium peroxide in the original dish and add this to the contents of the crucible. Dissolve any tungsten in the residue, that remains adhering to the dish, by heating with a little caustic soda solution and add this solution to that which is eventually obtained from the sodium peroxide fusion.

Heat the mixture in the nickel crucible with a very small flame until the flux is melted and continue the heating for about half an hour, heating just hot enough to keep the sodium peroxide liquid. After allowing the crucible to cool, place it in a beaker and add just enough water to cover the crucible. Heat the water to hasten the solution of the melt and when all is dissolved, remove the crucible and wash it out with hot water. Dilute the solution to about 200 c.c. and, if it appears green in color after the ferric hydroxide has settled out, add a little sodium peroxide from the blade of a knife; this serves to reduce sodium manganate to manganese dioxide. Allow the precipitate to settle completely and decant the clear solution through a filter, catching the filtrate in a 250-c.c. calibrated flask. Wash the precipitate in the beaker by pouring dilute sodium carbonate solution (2 g. per 100 c.c. water) upon it, allow the precipitate to settle, and decant the liquid through the filter. Repeat the washing several times until certain that all the sodium tungstate has been dissolved. Then cool the filtrate to room temperature and dilute to the mark. Mix the solution thoroughly and take an aliquot part for the further analysis, *e.g.*, two-fifths. Transfer the aliquot part of the solution to a beaker of about 350-c.c. capacity and precipitate with mercurous nitrate solution, exactly as described on p. 200. Treat the precipitate with sulfuric and hydrofluoric acids to remove the silica and continue the purification process as described on p. 201.

Instead of determining the chromium in the same sample, it is a little easier to take another aliquot part of the solution and determine the chromium in it according to p. 161. By multiplying the weight of chromium thus obtained by the factor

1.462, the corresponding weight of chromic oxide is obtained; deduct this from the weight of the impure tungsten trioxide.

If vanadium and molybdenum are present, these elements must be determined by methods to be described in the sections of this book which immediately follow. Corresponding quantities of V_2O_5 and MoO_3 must be deducted from the weight of impure tungsten trioxide.

If much phosphorus is present it must also be determined and allowance made. As a rule, however, the phosphorus content of tungsten steel is not over 0.03 per cent and the error resulting from neglecting it is not serious.

4. DETERMINATION OF TUNGSTEN IN MATERIALS INSOLUBLE IN ACID

(Ferro-tungsten, Metallic Tungsten)

Principle.—Iron alloys rich in tungsten may be analyzed by treatment with magnesia-sodium carbonate mixture (p. 125) provided the metal is brittle enough to be powdered. The tungsten is thereby converted to sodium tungstate which dissolves in water.

Procedure.—Mix from 1 to 3 g. of the finely powdered material in an agate mortar with six or eight times as much of Eschka mixture and heat in a platinum crucible for about an hour over a Méker burner. After cooling, extract the sintered mass in a beaker with hot water. If the solution is colored green by sodium manganate, add a little sodium peroxide and heat the solution to precipitate the manganese as dioxide. Filter off the sodium tungstate after allowing the precipitate to settle. Wash the residue on the filter with hot water, then transfer it to the same platinum crucible that was used before, smoke off the filter and heat again with about four times as much Eschka mixture as the original weight of the material. By this second heating of an hour, all the tungsten is converted to sodium tungstate unless the material was too coarse.

The well-washed residue may be used for the determination of iron and manganese.

Dilute the combined filtrates in a 500-c.c. calibrated flask and determine the tungsten in an aliquot part of the solution by the

method described on p. 196. If the filtrate obtained after ignition in the Eschka mixture is yellow, chromium is present; in such cases determine the chromium in another aliquot part of the solution (p. 161 *et seq.*) and deduct the corresponding weight of chromic oxide, Cr_2O_3, from the weight of impure tungsten trioxide. If vanadium and molybdenum are present, these elements must also be determined (pp. 212 and 193).

The method just described can be used for the determination of tungsten in metallic tungsten. In most cases, however, it is more important to know how much *metallic* tungsten an alloy contains rather than to know the total tungsten content, whether as metal or oxide, or combined with other non-metallic elements. By deducting the impurities from 100, the percentage of metallic tungsten can be found.

To determine the iron, manganese, lime, calcium and magnesia, fuse from 2 to 4 g. of the finely powdered metal with six times as much pure sodium carbonate, placing the mixture in a platinum crucible which already contains a little sodium carbonate on the bottom. Heat the fusion mixture an hour or two over a Bunsen burner keeping the contents of the crucible just below the fusion temperature. Finally raise the temperature and heat over the blast lamp for a short time. In this way a satisfactory fusion can be made. After dissolving the melt in water, and heating with a little sodium peroxide, the residue contains ferric oxide, manganese dioxide, nickel oxide, calcium carbonate and magnesium carbonate to the extent that these elements were present in the metallic tungsten. Some of the iron usually adheres to the sides of the crucible; dissolve this by warming with hydrochloric acid. All these substances in the residue are determined in the usual way. Further impurities are carbon, silicon, oxygen combined with iron or tungsten (for which a corresponding weight of ferric oxide or tungsten trioxide is deducted), phosphorus, chromium, vanadium, molybdenum, aluminium, water-soluble alkali tungstate, etc. These elements are determined as described in the corresponding chapters of this book.

CHAPTER XIII

VANADIUM

Small quantities of vanadium are often present in cast iron owing to the presence of vanadium in the iron ore. Vanadium is oxidized very easily and for that reason is used, like aluminium and titanium, as a deoxidizing agent in the manufacture of steel. When the amount of vanadium added is small, the greater part of it passes into the slag so that the finished steel is often greatly benefited and yet does not contain any vanadium. Special steels, on the other hand, often contain vanadium as an essential part of the alloy.

Vanadium, like nitrogen, forms five oxides: V_2O, V_2O_2, V_2O_3, V_2O_4 and V_2O_5. The first three are basic anhydrides. The last two oxides represent the types of vanadium compounds usually encountered in analytical chemistry. V_2O_4 is the anhydride of hypovanadic acid, $V_2O_4(OH)_4$, which is an amphoteric hydroxide. V_2O_4 itself is a blue powder which dissolves in concentrated mineral acids forming blue divanadyl salts.

$$V_2O_4 + 2H_2SO_4 = V_2O_2(SO_4)_2 + 2H_2O$$

If the solution of divanadyl salt is neutralized carefully, the insoluble hydroxide is formed but it dissolves readily in alkali solutions forming brown solutions containing compounds like $Na_2V_2O_5$ and $Na_2V_4O_9$, both being called hypovanadates.

V_2O_5 is the anhydride of vanadic acid which is similar to phosphoric acid in its chemical properties, although only slightly soluble in water. Like phosphoric acid, it forms ortho-salts, meta-salts and pyro-salts; of these the meta compounds are the most stable and the ortho ones the least so. Thus an aqueous solution of ortho vanadate is hydrolzyed, even in the cold, into the pyro-salt:

$$2Na_3VO_4 + H_2O \leftrightarrows Na_4V_2O_7 + 2NaOH$$

and on boiling the meta-salt is formed:

$$Na_4V_2O_7 + H_2O \leftrightarrows 2NaVO_3 + 2NaOH$$

The meta-, pyro-, and ortho-salts of the alkalies are colorless or pale yellow but polyvanadates, *e.g.*, the tetra- and hexa-vanadates, are a deep orange or red in color. Thus a pale yellow solution of a vanadate is colored orange on the addition of acid.

Vanadium also forms pervanadic acid, HVO_4, when hydrogen peroxide is added to an acid solution of a vanadate. This is reddish-brown in color and can be detected when only a trace of vanadic acid is contained in the solution. By heating with acid. the pervanadic acid decomposes into vanadyl salt.

The insoluble compounds of vanadium most used in the gravimetric determination of this element are, ammonium metavanadate, NH_4VO_3, which is practically insoluble in a concentrated solution of ammonium chloride; lead vanadate, which although practically insoluble in water is much more soluble in dilute nitric acid than is lead chromate, so that vanadic and chromic acids may be precipitated together or the latter alone precipitated in the presence of dilute nitric acid; and mercurous vanadate, $Hg_2(VO_3)_2$, which is white and soluble in nitric acid.

In the qualitative scheme of analysis, vanadium is usually classed with molybdenum in the arsenic-tin group. Hydrogen sulfide, however, will not give a precipitate of either V_2S_4 or V_2S_5 when introduced into an acid solution of divanadyl salt or of vanadic acid; the latter is reduced to vanadyl salt. If a strongly ammoniacal solution of a vanadate or hypovanadate is saturated with hydrogen sulfide, the color of the solution deepens and finally assumes a characteristic violet-red shade owing to the formation of soluble thiovanadate; on adding acid to the red solution a black precipitate of V_2S_5 and V_2S_4 is thrown down but the precipitation is not quantitative.

Vanadic acid is like phosphoric acid with regard to precipitation with ferric iron and aluminium. Thus in the qualitative scheme, vanadium may be precipitated by ammonium hydroxide as $V_2O_2(OH)_4$ if the vanadium is in the quadrivalent condition, or it may be precipitated as ferric or aluminium vanadate if these elements are present and the vanadium is quinquivalent.

Reducing agents (concentrated hydrochloric acid, sulfurous acid, hydrogen sulfide, alcohol, oxalic, citric and tartaric acids, sugar, etc.) reduce acid solutions of vanadic acid to blue divanadyl

salts. With hydriodic acid the reduction goes farther and a green solution of trivalent vanadic salt is obtained.

The volumetric methods for determining vanadium, and these are the most accurate for determining small quantities of this element, usually depend upon getting the vanadium entirely into the quadrivalent condition and measuring the volume of standard oxidizing solution necessary to convert the quadrivalent vanadium completely into the quinquevalent state. Referred to the old oxide theory, this is often regarded as the oxidation of V_2O_4 into V_4O_5. In reality, the reaction represents the oxidation of blue divanadyl salt into vanadic acid, H_3VO_4, or metavanadic acid, HVO_3. According to this conception the reduction and oxidation may be represented by the following equations:

$$2HVO_3 + H_2SO_3 + H_2SO_4 \rightarrow V_2O_2(SO_4)_2 + 3H_2O$$

$$5V_2O_2(SO_4)_2 + 2KMnO_4 + 12H_2O \rightarrow 2MnSO_4 + 2KHSO_4 + 10HVO_3 + 6H_2SO_4$$

or, in terms of the electrolytic dissociation theory:

$$2VO_3^- + SO_3^= + 6H^+ \rightarrow V_2O_2^{++} + SO_4^= + 3H_2O$$

$$5V_2O_2^{++} + 2MnO_4^- + 12H_2O \rightarrow 10VO_3^- + 2Mn^{++} + 24H^+$$

1. DETERMINATION OF VANADIUM BY THE PHOSPHOMOLYBDATE PRECIPITATION METHOD[1]

Principle.—In this method the vanadium is oxidized to vanadic acid and precipitated, together with phosphoric acid, by means of ammonium molybdate. The precipitate is filtered off and dissolved in hot, concentrated sulfuric acid. In the sulfuric acid solution, the vanadic acid is converted into pervanadic acid by treatment with hydrogen peroxide in the cold and the pervanadic acid upon further heating is decomposed into blue divanadyl salt. The latter is titrated with permanganate and vanadic acid formed.

Solutions Required.—*Nitric acid.*—Mix 1,000 c.c. of concentrated nitric acid (d. 1.42) with 1,200 c.c. of distilled water.

Strong Potassium Permanganate.—Dissolve 25 g. in 1 liter of water.

Sodium Bisulfite.—Dissolve 30 g. of solid in 1 liter of water.

[1] *Am. Soc. Testing Materials*, **1915**, 243.

Ammonium Phosphate.—50 g. in 1 liter of water.

Ammonium Molybdate.—See Phosphorus, p. 93.

Acid Ammonium Sulfate.—Pour 50 c.c. of concentrated sulfuric acid (sp. gr. 1.84) into 950 c.c. of distilled water, shake and add 15 c.c. of concentrated ammonium hydroxide (d. 0.90). Use at a temperature of 80°.

Standard Potassium Permanganate.—Dissolve 0.35 g. of potassium permanganate in 1,000 c.c. of water and standardize against pure sodium oxalate (p. 58). Since in the titration an atom of vanadium changes only one in valence, 1 c.c. of normal permanganate = 0.051 g. of vanadium. Since 1 c.c. of normal $KMnO_4$ = 0.067 g. of pure sodium oxalate, it is clear that the vanadium value can be obtained by multiplying the sodium oxalate value by the fraction 51/67 = 0.761. Adjust the solution for convenience so that 1 c.c. permanganate = 0.001 g. vanadium = 0.04 per cent V when 2.5 g. of steel is taken for analysis.

Procedure.—Dissolve 2.5 g. of steel in a 300-c.c. Erlenmeyer flask with 50 c.c. of nitric acid. Heat, and while boiling add 6 c.c. of the strong permanganate solution, continuing to heat until manganese dioxide precipitates. Dissolve the precipitate by the addition of small portions of sodium bisulfite solution and boil until the solution is clear and free from oxides of nitrogen. Add 5 c.c. of ammonium phosphate solution and 10 g. of ammonium nitrate, heat to boiling, remove from the hot plate and add immediately 50 c.c. of the ammonium molybdate solution. Let stand 1 min., then shake or agitate for 3 min. Filter the supernatant solution through an asbestos filter, washing three times with hot acid ammonium sulfate solution and drain by suction. Then place the flask containing the larger part of the precipitate under the funnel and treat the asbestos pad with successive portions of hot, concentrated sulfuric acid (d. 1.84). Heat the solution in the flask until all the precipitate is dissolved, add a few drops of nitric acid and evaporate until copious fumes of sulfuric acid are evolved. Cool, add hydrogen peroxide in small quantities, shaking after each addition, until the solution shows a brown color. Replace the flask on the hot plate and heat 4 or 5 min. longer and the solution becomes a clear green or blue, showing divanadyl salt.

If after this treatment the color of vanadyl salt is not obtained,

heat again till fumes of sulfuric acid are evolved, to remove traces of nitric acid which interfere with the reaction. Then cool and treat with hydrogen peroxide as before.

Finally cool the solution, dilute carefully with 100 c.c. of distilled water, heat to 80° and titrate with permanganate to a permanent pink.

2. DETERMINATION OF VANADIUM BY THE BLAIR METHOD[1]

The method is very similar to that recommended by J. R. Cain and L. F. Witmer when working at the U. S. Bureau of Standards. They precipitated vanadic acid with mercurous nitrate[2] instead of using lead acetate and accomplished the reduction of the vanadium by means of sulfurous acid, as indicated on p. 208.

Principle.—The vanadium is separated from the iron as in the previous method and from chromium by precipitation with sodium hydroxide. The vanadium is then precipitated in acetic acid solution by means of lead acetate. The lead vanadate is dissolved in hot hydrochloric acid, the vanadium reduced to vanadyl salt by boiling with hydrochloric acid and the vanadyl salt is oxidized with potassium permanganate. The reactions may be expressed as follows:

$$Pb_3(VO_4)_2 + 6HCl = 3PbCl_2 + 2H_3VO_4$$
$$2H_3VO_4 + 6HCl = 2VOCl_2 + 6H_2O + Cl_2$$
$$VOCl_2 + H_2SO_4 = VOSO_4 + 2HCl$$
$$5VOSO_4 + KMnO_4 + 11H_2O = 5H_3VO_4 + KHSO_4 + MnSO_4 + 3H_2SO_4$$

[1] BLAIR, A. A., *J. Am. Chem. Soc.*, **30**, 1228.

[2] For routine work, the American Society for Testing Materials sanctions the determination of vanadium without removal of chromium, using a blank determination with Cr added equivalent to the Cr content of the steel. In this case, after the removal of ether in the procedure of Blair, 25 c.c. of concentrated sulfuric acid are added and the solution is evaporated to fumes. After cooling, 25 c.c. of water and a slight excess of strong permanganate solution (p. 208) are added and the solution is boiled. Then 15 c.c. of concentrated hydrochloric acid are added and the solution is again evaporated until fumes of sulfuric acid are obtained. Finally, after again diluting with water, the vanadyl salt is titrated with permanganate at 60°.

Procedure.—Carry out the ether separation exactly as described on p. 73 and remove the dissolved ether by evaporating on the water bath. Add nitric acid in excess and evaporate to remove the hydrochloric acid. When the solution is almost sirupy, add 20 c.c. of hot water and heat with a few drops of sulfurous acid solution to reduce any chromic acid that may have been formed. Boil and slowly pour the hot solution, stirring vigorously, into a boiling solution of sodium hydroxide (100 g. NaOH to the liter; 1 c.c. of this solution will neutralize about 2.4 c.c. of nitric acid, d. 1.2). Boil the solution a few minutes, allow the precipitate to settle, filter, and wash the precipitate until it is free from alkali. The precipitate contains the hydroxides of chromium, nickel and iron, copper and manganese while the vanadium remains in the filtrate as sodium vanadate. To remove traces of chromium that may be left in the filtrate, slightly acidify with dilute nitric acid, make alkaline with sodium hydroxide and boil again. If any more precipitate is formed, filter, and make the filtrate acid with acetic acid. Heat the filtrate to boiling, add an excess of lead acetate solution (usually 10 c.c. is sufficient) and boil for several minutes. Filter off the precipitate of yellow lead vanadate and wash it with hot water. Dissolve the precipitate by pouring hot dilute hydrochloric acid through the filter.[1] Evaporate nearly to dryness, add 50 c.c. of hydrochloric acid (d. 1.2), and again evaporate nearly to dryness. Finally add 10 c.c. of concentrated sulfuric acid and evaporate until the acid fumes freely. Cool, dilute to 150 c.c., heat to between 60 and 70°, and titrate slowly with dilute permanganate solution.

Computation.—If n c.c. of f-normal permanganate were used in titrating the vanadium in a sample weighing s g., then as on p. 209,

$$\text{per cent V} = \frac{n \times f \times 5.10}{s}$$

NOTES.—Campagne[2] has shown that good results can be obtained by this reduction with hydrochloric acid when not more than 0.1 g. of vanadium is

[1] If there is much precipitate, remove the lead by evaporating to dryness, moistening the residue with hydrochloric acid, and treating with alcohol. Filter off the lead chloride and evaporate off the alcohol; the vanadium will then be present entirely as vanadyl salt.

[2] *Ber.*, **36**, 3104.

present. Gooch and Stockey[1] have also shown that the reduction by means of hydrochloric acid is practically complete. Rosenheim[2] and Holverscheidt,[3] however, have claimed that the results are a little low, and that the reduction by means of sulfurous acid is safer. With this reagent the reduction is accomplished by boiling the solution, which contains sulfuric acid, while passing sulfur dioxide through it until the solution appears a pure blue, showing that the vanadic acid has been reduced to vanadyl salt. Continue the boiling and replace the stream of sulfur dioxide with one of carbon dioxide, until the vapors when led into a dilute solution of potassium permanganate will no longer decolorize it. Then titrate the hot solution with permanganate.

This method may be carried out after a previous titration with permanganate, so that it may be used as a check upon the other method.

Müller and Diefenthaler,[4] in the analysis of ferro-vanadium, found that the reduction by means of hydrochloric acid alone did not always give dependable results. They found that much depended upon the exact manner in which the evaporation was conducted and that different values were obtained after evaporation in an Erlenmeyer flask than when an open porcelain evaporating dish was used. They regard the reduction with sulfurous acid as the standard method but find that nearly as good results can be obtained by evaporating with hydrochloric acid and alcohol. The procedure they recommended for the analysis of ferro-vanadium is as follows:

Weigh about 1 g. of the finely divided alloy into a covered beaker and dissolve it in a little concentrated nitric acid. Evaporate to remove the excess nitric acid, add a little concentrated hydrochloric acid and evaporate nearly to dryness to change the ferric nitrate into ferric chloride. Add 20 c.c. more of concentrated hydrochloric acid and 50 c.c. of alcohol and evaporate, by gently boiling the solution, to about 5 c.c. Rinse the solution into a calibrated flask and determine iron in one aliquot part and the vanadium in another.

Determine the iron by the iodometric method given on p. 170. The results are usually about 0.5 per cent too high.

Determine the vanadium by titrating the cold solution with permanganate, using the manganese sulfate reagent as in the determination of iron by the Zimmerman-Reinhardt method (p. 232).

3. DETERMINATION OF VANADIUM BY AN IODOMETRIC METHOD

Principle.—Vanadium, like manganese and many other metals, can be separated from ferric chloride in hydrochloric acid solution by shaking the solution with ether. If, however, the separation

[1] *Chem. News*, **87**, 133; *Z. anorg. Chem.*, **32**, 456.
[2] *Ann.*, **251**, 197.
[3] *Inaug. Diss.*, Berlin, 1890.
[4] *Z. anorg. Chem.*, **71**, 243 (1911).

is carried out exactly as described for manganese, it sometimes happens that a little vanadium follows the iron into the ether; this vanadium may be removed from the ether solution by shaking with hydrochloric acid (d. 1.1) that has been saturated with ether, and adding a few drops of hydrogen peroxide, which forms pervanadic acid, insoluble in ether.

The vanadium may be separated from manganese, nickel, etc., by an oxidizing fusion (*cf.* p. 76) and from chromium by heating with potassium acid tartrate mixture (p. 164). In the aqueous extract the vanadium may be determined iodometrically by the method of Holverscheit.[1] The vanadic acid, containing quinquevalent vanadium, is reduced by the action of hydrobromic acid to either hypovanadic acid or vanadyl salt, probably the latter, in which the vanadium is quadrivalent. The reaction may be expressed as follows:

$$2V^{+++} + 2Br^{-} = 2V^{+++} Br_2$$

or,

$$2HVO_3 + 2KBr + 6HCl = 2VOCl_2 + 2KCl + Br_2 + 4H_2O$$

The bromine is distilled into potassium iodide solution and the liberated iodine is titrated with standard thiosulfate solution. The equation shows that 1 atom of vanadium loses one valence charge and is equivalent to 1 atom of bromine; it follows, therefore, that 1 c.c. of normal sodium thiosulfate solution is equivalent to 0.0510 g. of vanadium.

Inasmuch as the vanadium content of iron and steel is usually very low, it is advisable to use an approximately fiftieth-normal solution, prepared by taking 100 c.c. of tenth-normal sodium thiosulfate, standardized as described on p. 63, 147 or 156, and diluting to exactly 500 c.c. in a calibrated flask. The titer of the well-mixed solution is then one-fifth of the original solution.

Necessary Apparatus and Solutions.—The Rothe shaking apparatus and ether-hydrochloric acid solutions are described on p. 71. For distilling off the iodine and catching the vapors in potassium iodide solution, the Bunsen apparatus shown in Fig. 25 is used.

Procedure.—Weigh out 10 to 15 g. of the material into a porcelain evaporating dish and dissolve in dilute nitric acid (d.1.2).

[1] Dissertation, Berlin, 1890.

Remove the silica by Method 3 (p. 121) or the determination may be hastened as described on p. 121. In the filtrate from the silica, remove the ferric chloride by shaking with ether as described on p. 88. To remove traces of vanadium from the ethereal solution of ferric chloride, shake the latter three or four times with the 10-c.c. portions of ether-hydrochloric acid (d. 1.10) and 3 to 5 drops of 3 per cent hydrogen peroxide solution, instead of with ether-hydrochloric acid alone.

Ether usually contains a little peroxide, and this suffices, when the vanadium content is low, to give a reddish-brown coloration to the aqueous solution first obtained on shaking with ether. If more vanadium is present the vanadium solution first obtained is bluish-green or blue. If much vanadium is present the ether solution will usually contain an appreciable quantity of vanadium; when this is the case, dark brown flocks will be noticed on adding the hydrogen peroxide to the olive-green ferric chloride solution in ether.

After the removal of the iron, treat the solution exactly as described on p. 75, finally fusing with sodium hydroxide and sodium peroxide, and dissolving the fused mass in water.

Filter off the oxides of manganese and nickel and boil the filtrate, which is yellow if chromium is present, to decompose the excess of peroxide. Neutralize the solution with dilute nitric acid and precipitate the vanadium with mercurous nitrate solution exactly as described under Chromium (p. 162). Test the colorless filtrate with more mercurous nitrate solution to see if the precipitation was complete. If no more precipitate is formed, acidify the filtrate with nitric acid and add a few drops of hydrogen peroxide; if all the vanadium was precipitated there will be no brown coloration of pervanadic acid. The precipitate contains all the vanadium and chromium together with some phosphorus. After filtering and washing the precipitate, ignite it together with the filter in a platinum crucible, fuse with potassium acid tartrate mixture (*cf.* Chromium, p. 164), and extract the product of the fusion with a little hot water.

If considerable residue was obtained after heating the mercurous salt, it is advisable to fuse this last residue of chromic oxide with potassium acid tartrate again. The fusion may be accomplished in the same way as before, or the chromic oxide may be

fused with pure sodium carbonate and then enough potassium acid tartrate added to reduce all the chromium to chromic oxide. Extract the fused product with hot water and add the solution to that previously obtained. Wash the residual chromic oxide and carbon with hot water until the soluble alkali salts are all dissolved.

Concentrate the aqueous solution of the sodium vanadate to about 35 c.c. and transfer it to the decomposition flask of the Bunsen apparatus (Fig. 25), washing out the beaker several times with a little water and keeping the total volume of liquid as small as possible.

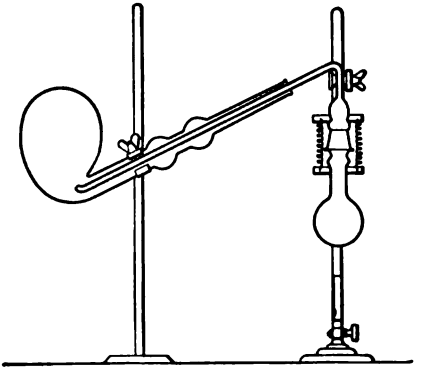


FIG. 25.

Neutralize the solution in the flask by the cautious addition of concentrated hydrochloric acid (free from chlorine) and add about 30 c.c. of the concentrated acid in excess to the solution which is now yellow in color. Introduce about 3 g. of pure potassium bromide and at once connect the apparatus as shown in the drawing, placing a concentrated solution of pure potassium iodide (from 5 to 10 g. free from iodate) in the receiver. Arrange the apparatus so that the receiver can be turned in the clamp to let air escape during the distillation. The tube which leads from the distilling flask to the iodine solution should have an opening from 1 to 2 mm. in diameter.

Gradually heat the liquid in the flask to boiling and allow the air to escape, from time to time, by turning the receiver. After the distillation begins, shown by the fact that the vapors are absorbed with a hissing noise, continue heating for about 10 min. longer. The yellow solution in the distilling flask changes to green and finally blue when all the quinquevalent vanadium has been reduced to the quadrivalent condition. Then, before taking the flame away, detach the receiver from the clamp and remove it from the delivery tubing; after this the flame may be withdrawn without danger of the solution sucking back. Cool the contents

of the receiver under running water, rinse it into an Erlenmeyer flask, and titrate the free iodine with sodium thiosulfate solution, adding starch solution toward the last. To make certain that there is no unchanged vanadate in the decomposition flask, fill the receiver with fresh potassium iodide solution and repeat the distillation.

Computation.—If n c.c. of f-normal sodium thiosulfate solution were used in titrating the vanadium in a simple weighing s g., then

$$\text{per cent V} = \frac{n \times f \times 5.10}{s}$$

4. DETERMINATION OF VANADIUM AFTER A FUSION

Principle.—The finely powdered material is fused with a suitable alkaline flux, the alkali vanadate thus formed is dissolved in water, and then determined as in the above methods. To make sure that the residue insoluble in water contains no vanadium, it is advisable to fuse it a second time.

If it is impossible to reduce the original material to a powder, it is best to treat first with nitric acid, evaporate the nitrates to dryness, convert them into oxides by ignition, and then carry out the fusion.

Procedure.—Mix 1 to 2 g. of the finely powdered material in an agate mortar with six times its weight of Rothe magnesia-sodium carbonate mixture (1 : 2) and heat the mixture in a platinum crucible as described on p. 125.

With samples which are not brittle enough to powder, dissolve 2 to 3 g. in a small porcelain dish with nitric acid (d. 1.2), evaporate the solution, heat to decompose the nitrates, and fuse the residue in a nickel crucible with 12 to 18 g. of sodium peroxide (*cf.* p. 165).

In both cases, extract the product of the fusion with water; if the solution is colored green by manganate, reduce the latter to manganese dioxide by adding a little sodium peroxide.

Then filter off the insoluble residue through an ashless filter, wash it thoroughly with hot water, and ignite the filter with its contents in a platinum crucible. Mix the residue with 3 to 6 g. of sodium carbonate, again fuse and extract with hot water, adding the solution to that previously obtained.

The combined filtrates contain all the vanadium as sodium vanadate in the presence of sodium phosphate, chromate, tungstate, etc. Neutralize the solution with nitric acid and treat with mercurous nitrate solution as described on p. 162.[1]

If the vanadium content is high, so that a large mercurous precipitate is to be expected, dilute the solution in a calibrated flask and use an aliquot part for the treatment with mercurous nitrate.

Filter off the precipitate, ignite, and fuse the oxides with sodium carbonate and acid potassium tartrate as described on p. 164. Extract the fusion with water, filter off the chromic oxide and carbon, and concentrate the filtrate to a small volume. Neutralize the solution with hydrochloric acid and distil with potassium bromide as described on p. 215.

Or, instead of determining the vanadium iodometrically, the aqueous solution which has been freed from chromium may be evaporated with hydrochloric acid and the reduced vanadyl salt determined by titrating with permanganate (*cf.* p. 211).

5. GRAVIMETRIC DETERMINATION OF VANADIUM[2]

Principle.—Ammonium metavanadate, NH_4VO_3, is insoluble in a cold, saturated solution of ammonium chloride. By ignition, it is changed into vanadium pentoxide, V_2O_5.

The ammonium chloride method of precipitating vanadium cannot be used in the presence of tungstate.[3] If chromate is present, some chromate is precipitated with the vanadium and some vanadium is not precipitated, so that in many cases the correct value is obtained by compensation. The presence of phosphate, arsenate, molybdate or sulfate does not seriously interfere.

Procedure.—If tungsten is present start the analysis according to Method 3, dissolving about 5 g. of the material, removing the silica and tungsten from hydrochloric acid solution, the iron by shaking with ether, and fusing in a platinum dish, etc.

[1] If no chromium is present, the aqueous solution is colorless. In such a case, the vanadium can be determined directly without previous precipitation with mercurous nitrate. Acidify the solution at once with hydrochloric acid and transfer to the evolution flask.

[2] *cf.* GOOCH and GILBERT, *Z. anorg. Chem.*, **32**, 175 (1902); CAMPAGNE, E., *Ber.*, **1903**, 3164.

[3] ROSENHEIM, *Z. anorg. Chem.*, 32, 181 (1902).

In the absence of tungsten, Method 4 may be used for starting the analysis.

Ignite the mercurous nitrate precipitate, obtained by either of these methods, and remove the chromium by the sodium carbonate and potassium acid tartrate fusion. Neutralize the aqueous extract of the fusion with nitric acid and decolorize the yellow solution by adding a little ammonia and heating. Estimate the approximate volume of the solution and, if it seems advisable, concentrate it somewhat.

To the cold solution add, all at once, 2.5 g. of pure ammonium chloride for each 10 c.c. of solution and stir vigorously to dissolve the salt. The solution becomes colder, a turbidity forms, and gradually white flocks of ammonium metavanadate are precipitated. When this procedure is followed there is little tendency for the precipitate to attach itself to the sides of the beaker.

Allow the solution to stand at least 8 hr., then filter and wash the precipitate with cold, 25 per cent ammonium chloride solution. Ignite the precipitate in a platinum crucible, finally melting the vanadium pentoxide.

After weighing the oxide, V_2O_5, boil it with a little concentrated sodium hydroxide solution. It should dissolve in the alkali without leaving any residue. The purity of the precipitate may be tested by pouring the solution into the Bunsen apparatus, acidifying and distilling with potassium bromide, as described on p. 215.

Computation.—If p g. of vanadium pentoxide were obtained from a sample weighing s g., then

$$\text{per cent V} = 56.04\frac{p}{s}$$

Test Analysis.—(*a*) *Experiments with Sodium Vanadate Solution.*—Fifty cubic centimeters of the solution were treated with mercurous nitrate solution and on ignition 0.3051 g. of V_2O_5 were obtained.

Ten cubic centimeters of the solution required 6.65 c.c. of sodium thiosulfate solution; according to this, 50 c.c. = 0.3030 g. V_2O_5.

When using 25 and 50-c.c. portions of the solution, the results obtained by iodometric titration corresponded in each case to 0.3034 g. V_2O_5 in 50 c.c.

Twenty-five cubic centimeters of solution precipitated with ammonium chloride gave 0.1528 g. V_2O_5; 50 c.c. of solution would contain, therefore, 0.3056 g. V_2O_5.

The ammonium chloride process was carried out with 25-c.c. portions of sodium vanadate solution in the presence of 1-g. portions of each of the following salts: potassium acetate, sodium nitrate, sodium sulfate, sodium phosphate, potassium arsenate, ammonium molybdate, potassium chromate and sodium tungstate. With each of the first five salts the values ranged from 0.1520 to 0.1528 g. of V_2O_5, which agreed satisfactorily with the theoretical value, 0.1526 g. V_2O_5. With ammonium molybdate, the precipitation of the vanadium was complete but the precipitate contained about 2 mg. of impurity. With the chromate about the same excess weight was obtained and the filtrate contained a little vanadium. In the presence of tungsten, the precipitate weighed about 3 mg. too little and contained tungsten.

(*b*) *Separation of Vanadium and Iron by the Ether Process.*—Ten cubic centimeters of a vanadium solution, prepared by dissolving vanadium pentoxide in hydrochloric acid, contained 0.2300 g. V_2O_5.

When mixed with ferric chloride solution, corresponding to 3.2 g. of metallic iron, the ammonium chloride precipitate yielded 0.2304 g. V_2O_5. With ferric chloride corresponding to 6.5 g. of iron, the value was 0.2295 g. V_2O_5.

(*c*) *Determination of Vanadium in Different Materials.*—The analysis of a cast iron by the ammonium chloride process, using 4-g. samples, gave 0.029 per cent and 0.025 per cent V.

Another specimen of cast iron was analyzed by Method 1*a* and the values obtained with 5-g. samples were 0.139 per cent and 0.133 per cent V.

An alloy steel containing tungsten, chromium, molybdenum and vanadium was analyzed by Method 1*a* and the values obtained with 5-g. samples were 2.14 and 2.17 per cent V.

CHAPTER XIV

ALUMINIUM

In the manufacture of ingot iron and mild steel, aluminium is often added for the purpose of deoxidizing the molten metal. Aluminium is present in iron, therefore, chiefly in the form of its oxide. If more aluminium is added than is necessary to combine with all the oxygen, then some of it will remain in solid solution with iron. At the present time there is no absolutely dependable analytical test to determine whether the small quantity of aluminium usually found is present as oxide or as metal. Certain special alloys, *e.g.*, aluminium steel, are certain to contain metallic aluminium.

Principle.—Aluminium, like manganese, chromium, nickel, etc., can be separated from iron by the Rothe method of shaking the chlorides in hydrochloric acid solution with ether. In determining the aluminium by precipitation as aluminium hydroxide from dilute acetic acid solution, it is necessary to bear in mind that the phosphorus from the steel is likely to be precipitated at the same time as aluminium phosphate;[1] for this reason it is advisable to precipitate the aluminium intentionally as aluminium phosphate.

Procedure.—Weigh from 5 to 10 g. of steel into a porcelain dish and dissolve it in 60 to 120 c.c. of concentrated hydrochloric acid. Evaporate the solution to dryness and remove the silica according to Method 1,[2] p. 115. Avoid dehydrating the silica at too high a temperature on account of the danger of volatilizing aluminium chloride; there will be no loss in a hot closet at 135°. The deposited silica is likely to retain a little aluminium.[3] After treating the silica with hydrofluoric and sulfuric acids, therefore, fuse the residue with a little sodium carbonate and determine the aluminium as hydroxide or as phosphate as described for the main determination.

[1] When steel is dissolved in hydrochloric acid, some of the phosphorus is evolved as phosphine.

[2] Or by method 3, p. 121; *cf*, *d*, p. 88.

[3] If the residue contains much aluminium this indicates that it was originally present as oxide.

Concentrate the filtrate from the silica by evaporating until a crust of crystals begins to separate on the edges of the solution; then add, to the hot solution, dilute nitric acid (d.1.2) in small quantities and cover the dish with a watch-glass. When the oxidation of the iron is complete, which is recognized by the fact that no more oxides of nitrogen are evolved and the solution in the dish becomes transparent,[1] remove the watch-glass and evaporate the solution to dryness. To remove any remaining nitric acid, take up the residue with concentrated hydrochloric acid and evaporate to the consistency of sirup. Shake the solution of the chlorides with ether in the usual manner (*cf.* p. 73).

Evaporate the aqueous chloride solution, which is nearly free from iron, to remove the ether and dissolve the residue in a little hydrochloric acid. Dilute the solution until it contains about 25 c.c. of water for each c.c. of hydrochloric acid (d. 1.12) present, precipitate the copper by adding a little hydrogen sulfide water to the hot solution and filter off the copper sulfide.

Add a few c.c. of dilute sulfuric acid to the filtrate and evaporate the solution in a porcelain dish until fumes of sulfuric acid are evolved; it is necessary to heat over a free flame toward the last. The reason for transforming the chlorides into sulfates is because the aluminium precipitate filters better when deposited from a sulfate solution. Dissolve the residue of sulfates in water, heating till all is dissolved, and dilute to about 100 c.c. in a 200 to 250-c.c. beaker. Add ammonia until the solution is alkaline to litmus paper and at once redissolve the aluminium hydroxide with as little dilute sulfuric acid as possible. A little brown oxide of manganese usually remains undissolved; take this up by adding about 1 c.c. of sulfurous acid. To the slightly acid solution, add 2 or 3 c.c. of neutral ammonium acetate solution (100 g. in 500 c.c. of water); the solution should still have a slightly acid reaction.

Heat the solution to boiling, which causes all the aluminium to precipitate together with some impurity. After allowing the precipitate to settle, filter and wash the precipitate with water containing a little ammonium acetate. Finally rinse back the

[1] When the nitric acid is first added, a dark brown compound with NO and ferrous salt is formed. This disappears when no more ferrous salt is present.

precipitate into the original beaker and dissolve it in as little sulfuric acid as possible, heating on the water bath to aid the solution. Repeat the precipitation with ammonium acetate and filter through the same filter, washing as before.

The filtrate now contains all the nickel and manganese and the precipitate consists chiefly of aluminium hydroxide and phosphate. Rinse the precipitate back into the beaker, dissolve it once more in dilute sulfuric acid, avoiding an excess, add 1 or 2 c.c. of ammonium phosphate solution (100 g. in 500 c.c. of water) and reprecipitate the aluminium by adding a very slight excess of ammonia to the boiling hot solution.

After the precipitation is complete, acidify slightly with acetic acid, heat to boiling, filter and wash the precipitate with hot water containing a little ammonium acetate. Ignite and weigh as $AlPO_4$.

When perfectly pure, the aluminium phosphate is white. If small amounts of chromium are present in the original metal, it is precipitated as chromic phosphate with the aluminium phosphate and the precipitate has a grayish or green tint. In such cases, fuse the ignited precipitate with a little sodium carbonate and determine the chromic acid by treating the acid extract of the melt with potassium iodide and titrating the iodine set free with standard thiosulfate solution (*cf.* p. 161). Compute the quantity of chromic phosphate corresponding to this titration and subtract it from the weight of the phosphate precipitate previously obtained.

When the Rothe separation is successfully accomplished, not more than 1 or 2 mg. of iron should follow the aluminium into the aqueous layer obtained in the treatment with ether. In such cases the aluminium precipitate is not contaminated with iron, which is in the ferrous condition owing to the addition of sulfurous acid. If, however, the first precipitation of hydroxides obtained in the above procedure is plainly contaminated with iron, it is advisable to evaporate the sulfuric acid solution to dryness in a platinum dish, heat until the free sulfuric acid is all expelled, and fuse with a little caustic soda and sodium peroxide, as described under Manganese, p. 76. Neutralize the aqueous extract of the melt with sulfuric acid, remove the sodium salts by precipitating the aluminium twice with ammonia, and finally precipitate the aluminium phosphate as described above.

Computation.—If a sample of steel weighing s g. gives p. g. of aluminum phosphate, then

$$\text{per cent Al} = \frac{p \times \text{Al} \times 100}{\text{AlPO}_4 \times s} = \frac{22.19p}{s}$$

Test Analysis.—(1) *Experiments with Aluminium Chloride Solution.*—Twenty cubic centimeters of an aluminium chloride solution free from phosphoric acid gave, in two experiments by precipitation with ammonium acetate and weighing as Al_2O_3, the values 0.0464 and 0.0465 g. Al.

The same quantities of solution analyzed by precipitation as $AlPO_4$ gave the values 0.0475 and 0.0477 g. Al.

In two other experiments, in which ferric chloride equivalent to 5 g. of metallic iron was added in each case, the values 0.0491 and 0.0475 g. Al were obtained.

2. *Analysis of Aluminium Steel. Sample* 1.—Duplicate determinations in 5-g. samples gave the values 0.23 and 0.25 per cent Al. The silica precipitate contained no aluminium.

Sample 2.—(*a*) In the analysis of a sample weighing 5 g., a precipitate of aluminium phosphate weighing 0.0687 g. was obtained in the main analysis. This precipitate was contaminated with chromium and the subsequent titration with sodium thiosulfate showed 0.0036 g. of $CrPO_4$. Subtracting this from the original weight of the phosphate precipitate, the value 0.292 per cent Al was obtained.

The silica precipitate was tested for aluminium and additional aluminium amounting to 0.033 per cent obtained, making the total Al content = 0.33 per cent.

(*b*) A duplicate determination with similar results gave 0.34 per cent Al.

Accuracy of Aluminium Values and Permissible Deviations

The values reported in samples containing up to 1 per cent Al should be accurate to within 0.05 per cent, provided a careful blank is made with the same quantities of reagents as used in a regular analysis.

CHAPTER XV

ARSENIC

Arsenic occurs quite commonly in iron ores and for this reason there is likely to be some arsenic in most samples of iron and steel; von Reis found in some cases as much as 0.08 per cent arsenic.

Inasmuch as arsenic tends to injure the metal, the knowledge of the arsenic content is of importance in judging the value of a given material. A previous chapter has shown the effect of arsenic on the determination of phosphorus so that a knowledge of the arsenic content is of importance to the chemist in helping him to choose a suitable method for that determination.

Principle.—When iron or steel is dissolved in *nitric acid* the arsenic is converted into arsenic acid. On evaporating to dryness and decomposing the nitrates all the arsenic remains in the residue as arsenate.

From the hydrochloric acid solution of the residue it is possible to distil off arsenic trichloride after reducing the iron to the ferrous state by means of a suitable reducing agent.[1] One of the most satisfactory reducing agents in this case is cuprous chloride. The reduction process can then be represented by the ionic equation

$$Fe^{+++} + Cu^{+} = Fe^{++} + Cu^{++}$$

Accordingly, 56 parts by weight of iron require 99 parts by weight of cuprous chloride.

Procedure.—Dissolve 10 to 12 g. of the iron or steel in a 500-c.c. round-bottomed flask by the gradual addition of nitric acid (d. 1.2), and heating over the Bunsen flame. Evaporate to dryness (*cf.* p. 88) and heat the residue until no more nitrous fumes are evolved. Cool and dissolve the residue in 80 to 100 c.c. of concentrated hydrochloric acid, warming very gently and rotating the liquid about in the flask. The liquid must not be heated to boiling as there is a chance of some arsenic being lost thereby.

[1] Some reducing agents, *e.g.*, stannous chloride and sodium hypophosphite, reduce a part of the arsenic to the metallic condition and others, *e.g.*, zinc and iron, reduce it to arsine, AsH_3. Ferrous salts reduce quinquevalent arsenic to the trivalent state.

For each 10 g. of sample, add 18 g. of pure, arsenic-free cuprous chloride to the distilling flask, Fig. 26, pour upon it the hydrochloric acid solution of the sample and wash out the contents of the original flask with hydrochloric acid (d. 1.12). With the apparatus all in place, heat the contents of the distilling flask to boiling and catch the distillate in a 500 to 600-c.c. beaker. When only about 50 c.c. of liquid remain in the flask, stop heating, add 50 c.c. of concentrated hydrochloric acid (sp. gr. 1.2) and carefully distil again. These two distillations are sufficient to volatilize all the arsenic as trichloride.

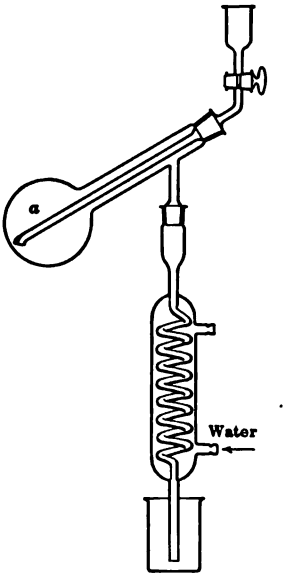


FIG. 26. — Apparatus for arsenic determination.

Dilute the strongly acid distillate with an equal volume of water, saturate it with hydrogen sulfide and allow the beaker to stand over night under a bell jar.

Filter off the precipitate of arsenic trisulfide through a small, well-running filter and wash with water until the washings are no longer acid. Rinse the precipitate into a small porcelain dish and dissolve the residue on the filter with ammonia, washing thoroughly with water containing ammonia. Concentrate the solution to remove the excess of ammonia and evaporate to dryness after adding concentrated nitric acid. Add a few drops of concentrated nitric acid, to help oxidize the residual sulfur, and evaporate on the steam bath. Dissolve the residue of arsenic acid in a little water, filter through a small filter and concentrate the filtrate, in a small beaker, to a volume of 10 to 20 c.c. Add 2 or 3 c.c. of magnesia mixture (*cf.* p. 93), half the solution's volume of ammonia water (d. 0.96) and stir vigorously with a glass rod. The precipitate of magnesium ammonium arsenate soon begins to form. After a short time add a little more magnesia mixture to see if any further precipitation takes place. Finally add alcohol corresponding to one-fourth the volume of the liquid and allow the precipitate to stand over night.

Filter off the precipitate through a weighed Gooch or Munroe crucible and wash with 2.5 per cent ammonia to the disappearance of chlorides. Dry the crucible and its contents at 110° and then heat it in air bath (*cf.* Fig. 17, p. 83), raising the temperature very gradually until a light red heat is obtained. Cool in a desiccator and weigh as magnesium pyroarsenate, $Mg_2As_2O_7$.

Computation.—If s is the weight of the sample and p the weight of the ignited precipitate, then

$$\frac{2As \times p \times 100}{Mg_2As_2O_7 \times s} = \frac{48.27p}{s} \text{ per cent As}$$

TEST ANALYSES

Experiments with an Arsenic Solution of Known Arsenic Content

Duplicate determination gave the values 0.0338 and 0.0332 g. $Mg_2As_2O_7$ in 10 c.c. of the arsenic solution. Experiments were carried out with 10 c.c. of the arsenic solution added to 5 g. of Kahlbaum's pure reduced iron (free from arsenic) and the weights of magnesium arsenate obtained were 0.0326 and 0.0328 g.

Experiments with Commercial Iron and Steel

No.	Material tested		Weight taken in grams	Weight of $Mg_2As_2O_7$	Per cent arsenic
1	Pig iron	*a*	5	0.0034	0.033
		b	5	0.0035	0.034
2	Siemens-Martin steel	*a*	5	0.0024	0.023
		b	5	0.0026	0.025
3	Siemens-Martin steel	*a*	5	0.0066	0.064
		b	5	0.0054	0.052
4	Siemens-Martin steel	*a*	10	0.0128	0.062
		b	10	0.0106	0.051

Accuracy of the Process.—The arsenic content of iron and steel up to 0.3 per cent As can be determined with an accuracy such that the results are probably correct to within about 0.01 per cent. It is necessary, however, to test all the reagents used by running a blank experiment. This is especially necessary because most hydrochloric acid contains traces of arsenic.

CHAPTER XVI

COBALT

Cobalt is usually present to some extent in all samples of iron and steel that contain nickel. In some special cases this element is an intentional constituent.

DETERMINATION OF COBALT AS SULFATE

Principle.—The complex thiocyanates of nickel and cobalt may be separated from one another by treatment with a mixture of amyl alcohol and ether.[1]

Apparatus and Solutions Required

1. *Rothe shaking funnel* (Fig. 13, p. 71).

2. *Amyl alcohol-ether* mixture. Mix 25 parts by volume of ether with 1 part of amyl alcohol.

Procedure.—If the nickel content is fairly high, weigh out about 5 g. of the original metal, or 10 g. if the nickel content is low. Deposit the nickel and cobalt electrolytically, as described on p. 178, and weigh the deposit.

Dissolve the deposited nickel and cobalt in a little concentrated nitric acid (d. 1.42) and carefully rinse off the electrode. To remove the excess of acid, evaporate the solution of nickel and cobalt nitrates just to dryness in a porcelain dish and dissolve the residue in a little water. For each 0.1 g. of metal present, add 4 g. of pure ammonium thiocyanate,[2] NH_4CNS, to the concentrated solution of cobalt and nickel nitrates. Dissolve the salt by means of a little water. It is essential to have a saturated solution at this point; if necessary, concentrate it by

[1] Rosenhain and Huldschinsky (*Ber.*, **34**, 2,050 (1901)) first proposed the quantitative application of Vogel's sensitive test for cobalt in the presence of nickel (*Ber.*, **12**, 2,314 (1879)).

[2] Commercial ammonium thiocyanate is often impure. It is absolutely necessary that no weighable residue should be obtained on heating the salt.

evaporation on the water bath. Transfer the concentrated solution to the upper bulb of the Rothe shaking funnel and rinse out the evaporating dish with a little saturated ammonium thiocyanate solution. Then add 60 to 80 c.c. of the amyl alcohol-ether mixture and shake vigorously. After the mixture has become perfectly quiet, the upper layer in the funnel is a beautiful blue even when only a little cobalt is present.[1] The cobalt is present in the ether layer as complex ammonium cobalti-thiocyanate and the nickel remains in the aqueous solution as simple thiocyanate. Allow the lower layer in the upper bulb of the funnel to run into the lower bulb and rinse the former with a little saturated ammonium thiocyanate solution. Add 10 c.c. more of saturated ammonium thiocyanate solution to the contents of the upper bulb and 40 c.c. of the ether mixture to the lower bulb and again shake vigorously. In this way the remainder of the nickel in the upper bulb is washed away from the ether and a little cobalt in the lower bulb is dissolved by the ether. Allow the liquids to stand until two layers are well separated in each bulb, and then transfer the green nickel solution in the lower bulb to a beaker and wash out the stopcock boring, etc., with a little ammonium thiocyanate solution. Then transfer the aqueous layer in the upper bulb to the lower bulb, and rinse the upper bulb with a little ammonium thiocyanate solution. Add 5 or 10 c.c. of dilute sulfuric acid (1:10) to the upper bulb, close the stopcock and shake well. The blue color of the amyl alcohol-ether mixture will now disappear and the cobalt will pass into the dilute sulfuric acid solution, imparting a pink color to it. The aqueous thiocyanate solution in the lower bulb contains traces of nickel. Allow it to flow into the beaker and rinse the bulb in the usual manner. Then transfer the cobalt sulfate solution in the upper bulb into the lower bulb and rinse the ether-alcohol remaining in the upper bulb with a few drops of dilute sulfuric acid. By shaking, the blue ether solution in the lower bulb is now decolorized.[2] Transfer the sulfuric acid solution of cobalt sulfate to a weighed porcelain crucible, rinse the ether-alcohol mixture in each bulb

[1] If a little iron is present the red color of ferric thiocyanate causes a composite colored layer and the iron contaminates the final cobalt sulfate.

[2] Usually the ether is colored reddish-brown by a little ferric thiocyanate.

with small portions of dilute sulfuric acid and add the washings to the contents of the crucible. Evaporate to dryness and heat to destroy organic matter and finally to remove the excess of sulfuric acid, as described under Manganese, p. 82. Weigh the pink cobalt sulfate and then test it for impurities. Dissolve it in a little water and add ammonia until the solution is weakly ammoniacal. If a precipitate of ferric hydroxide is formed, filter it off and weigh it. Add dimethylglyoxime solution, drop by drop, as long as any precipitate continues to form. Allow the solution to stand ½ hr. in a warm place and then filter off the precipitate of nickel salt upon a small filter. Wash it thoroughly with hot water, ignite it and weigh as nickelous oxide, NiO.

The quantity of cobalt present is computed by deducting from the original weight of cobalt sulfate, the weight of ferric oxide[1] obtained, and of nickel sulfate corresponding to the weight of oxide obtained after igniting the glyoxime precipitate.

To weigh the cobalt itself after purification, evaporate the filtrate from the nickel precipitate in a weighed porcelain crucible, ignite the residue after moistening it with a little nitric acid and a drop of sulfuric acid, and heat to constant weight as described under Manganese, p. 82. Or, the cobalt sulfate solution may be dissolved in water and the ammoniacal solution electrolyzed as described under Nickel, p. 178.

Computation.—If p represents the weight of pure cobalt sulfate obtained in the analysis of s g. of metal, then

$$\text{per cent Co} = \frac{38.03\ p}{s}$$

Test Analyses.—(1) *Separation of Nickel and Cobalt in Solutions of Pure Salts.*—Twenty-five-cubic-centimeter portions of a nickel chloride solution containing 0.0245 g. nickel were mixed with 25-c.c. portions of cobalt chloride solution containing 0.0110 g. cobalt. The cobalt was determined as sulfate according to the above directions and in three experiments the results obtained were 0.0115 and 0.0114 and 0.0122 g. cobalt. The cobalt sulfate obtained in the third experiment was impure. It was dissolved and the ammoniacal solution electrolyzed; 0.0114 g. cobalt was then obtained.

[1] Ferric sulfate changes to ferric oxide and sulfuric anhydride at temperatures at which nickel, cobalt and manganese sulfates are more stable.

2. *Analysis of Nickel Steel.*—The nickel and cobalt were determined together by the electrolytic method described on p. 178. The results of two experiments gave the values 23.50 and 23.46 per cent Ni + Co. From the electrolytic deposit, the impure cobalt sulfate obtained by the above method indicated 0.66 and 0.67 per cent Co but after dissolving the sulfate and determining the cobalt electrolytically the results were 0.38 and 0.39 per cent Co. The values obtained by deducting the weight of the nickel as determined by precipitation with dimethylglyoxime from the weight of the cobalt and nickel deposit, averaged 0.51 per cent.

3. *Cobalt Content of Commercial Nickel.*—Duplicate determinations of the cobalt content of a sample of commercial nickel gave the values 0.88 and 0.89 per cent cobalt.[1]

[1] Commercial nickel sometimes contains a little zinc. This will come down with the cobalt in the electrolytic determination and will also follow the cobalt in the potassium thiocyanate separation.

CHAPTER XVII

TITANIUM

Pig iron prepared from ores containing titanium often contains small quantities of this element. Moreover, titanium, like aluminium, is used as a deoxidizing agent and in some cases a little of the titanium gets into the metal in this way. Usually, however, the quantity of titanium used is regulated so that all of it goes into the slag.

Ferro-titanium and manganese-titanium are the principle alloys of titanium that are used in metallurgical operations.

1. DETERMINATION OF TITANIUM IN MATERIALS SOLUBLE IN ACID

Principle.—Titanium may be freed from the greater part of the iron by means of the Rothe ether separation (p. 71). After the ether treatment, the solution contains manganese, nickel, chromium, possibly some other metals and phosphoric acid besides the titanium and a little of the iron.

The titanium may be precipitated from such a solution by boiling an acetic acid solution[1] containing ammonium acetate and something to keep iron in the ferrous condition, but in most cases it is necessary to purify the titanium dioxide that is obtained by such a procedure. The weight of the impurities is deducted from the weight of impure titanium dioxide. The titanium may also be determined colorimetrically, or, if the titanium content is not too low, it may be determined by a volumetric process.[2]

Apparatus and Solutions Required.—

FOR THE ETHER TREATMENT:

Rothe shaking funnel, Fig. 13, *p.* 71.

Hydrochloric acid (*d.* 1.10).

Ether-hydrochloric Acid Solutions.—One solution is made by adding ether to concentrated hydrochloric acid (d. 1.2) until a layer of ether is formed after shaking, and the other solution is prepared from dilute hydrochloric acid (d. 1.10), in the same way.

[1] *cf.* BARNEBEY and ISHAM, *J. Am. Chem. Soc.*, **32**, 957 (1910).

[2] *cf.* HINRICHSEN, *Chem. Ztg.*, **31**, 738 (1907).

FOR TITRATING THE TITANIUM:

Ferric Chloride Solution.—Moisten 27 g. of pure ferric chloride crystals ($FeCl_3 \cdot 6H_2O$) with 10 c.c. of hydrochloric acid (d. 1.12), dissolve by warming with water and dilute the solution to 1 liter. The hydrochloric acid is necessary to prevent hydrolysis of the ferric chloride, whereby a basic chloride is precipitated which makes the solution unfit for use.

The ferric chloride solution may be standardized against tenth-normal sodium thiosulfate solution (*cf.* p. 171) or against tenth-normal permanganate (p. 172).

To standardize against sodium thiosulfate solution, measure out by means of a burette or pipette 35 to 50 c.c. of the ferric chloride solution into a 200-c.c. Erlenmeyer flask and concentrate to about 15 c.c. Add 2 c.c. of dilute hydrochloric acid (d. 1.12), and a solution of 3 g. potassium iodide dissolved in a little water; the potassium iodide must be free from iodate and its aqueous solution should remain colorless upon the addition of a little hydrochloric acid.[1] By means of hydriodic acid, ferric ions are reduced to ferrous ions and iodine is set free:

$$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$$

The iodine is titrated with tenth-normal sodium thiosulfate solution, adding starch solution toward the last. To reduce traces of ferric chloride that still remain in the solution, heat to 50°, or 60° at the most, cool to room temperature by running cold water upon the flask, add a little more starch solution and finish the titration with sodium thiosulfate.

To standardize against potassium permanganate, the Zimmermann-Reinhardt method[2] is suitable. Measure out, by means of pipette or burette, 25 to 50 c.c. of the ferric chloride solution into a small beaker, add 10 c.c. of hydrochloric acid (d. 1.12), and heat the solution nearly to boiling. Place the beaker on a piece of white filter paper and add stannous chloride solution (50 g. stannous chloride crystals, and 100 c.c. concentrated hydrochloric acid; heat till dissolved and dilute with water to 1 liter), drop by drop, until the yellow color of ferric chloride disappears from the hot solution. Take pains not to add a single drop of the stannous

[1] If iodine is liberated, an allowance for this must be made in the analysis.

[2] ZIMMERMANN, *Ber.*, **14**, 779 (1881); REINHARDT, *Chem-Ztg.*, **13**, 323 (1884).

chloride in excess of the quantity necessary to render the solution colorless. If more is used by accident, add a few drops of potassium permanganate solution to oxidize the excess stannous chloride and enough of the iron to give a slight yellow color (ferric chloride) to the solution and repeat the reduction with stannous chloride. Cool the solution to room temperature and quickly add 10 c.c. of mercuric chloride solution (50 g. in one liter of water). Allow the solution to stand 5 min. to complete the reaction between the excess stannous chloride and the mercuric chloride, whereby a silky precipitate of mercurous chloride is formed, then dilute to about 400 c.c. and add 20 c.c. of acid manganese sulfate solution (prepared by dissolving 67 g. of manganous sulfate crystals, $MnSO_4 \cdot 4H_2O$, in 500 c.c. water, adding 138. c.c. of phosphoric acid (d. 1.7), and 130 c.c. of sulfuric acid (d. 1.84), and diluting to 1 liter). After the addition of the manganese sulfate solution, titrate the ferrous solution slowly with tenth-normal permanganate. At no time should the solution of permanganate be added faster than the drops can be counted and it is important at the start and finish not to add a drop of permanganate until the color produced by the previous drop has disappeared entirely.

This method of standardization gives good results with a little practice. It is necessary to add the manganese sulfate solution as otherwise the dilute hydrochloric acid is oxidized by the permanganate in the presence of ferrous salt, and the results of the standardization will be too low on account of the use of too much permanganate. It is important to follow the directions very carefully.

Procedure.—Weigh out 10 to 15 g. of the iron or steel into a porcelain dish, and dissolve it in nitric acid (d. 1.18), using about 12 c.c. of acid for each gram of sample. Evaporate the solution to dryness, take up in hydrochloric acid and remove the silica in the usual way (p. 121). The silica carries down a little titanium dioxide with it. After volatilizing the silicon as tetrafluoride, therefore, fuse the residue with sodium carbonate, dissolve the melt in hydrochloric acid (d. 1.12) and add the solution to the filtrate from the silica.

Concentrate the solution and remove the ferric chloride as completely as possible by the ether method (p. 71). The pres-

ence of titanium is often betrayed by the hydrochloric acid solution becoming somewhat turbid after the first shaking with ether and more turbid after the second shaking, when flakes of titanium dioxide are deposited sometimes. Such precipitates are often colored pale yellow by a little peroxide in the ether. If the titanium content is low, a clear solution is obtained which is usually brownish-yellow on account of the formation of a little pertitanic acid by peroxide in the ether. The precipitation of titanium dioxide during the ether treatment is due to hydrolysis and is caused by the fact that ether removes some of the hydrochloric acid which was necessary to prevent hydrolysis;[1]

$$Ti^{++++} + 4H_2O \rightleftarrows Ti(OH)_4 + 4H^+$$

Under the proper conditions, the quantity of iron remaining with the titanium after the ether separation in the aqueous solution is very small. Evaporate off the dissolved ether by heating on the water bath and continue the evaporation to dryness. Add a little concentrated hydrochloric acid to the residue, whereby some of the titanium remains undissolved as TiO_2, dilute to 150 c.c. without filtering and add 3 g. of solid ammonium acetate. Heat the solution to boiling and keep gently boiling for a few minutes. All the titanium is then precipitated as dioxide contaminated with ferric basic acetate. Allow the precipitate to settle and then filter. Test the filtrate with hydrogen peroxide to see if any titanium remains. If so, boil the solution 15 min. longer. Wash the precipitate with water containing ammonium acetate, ignite and weigh. The precipitate is almost always contaminated with some iron. The true titanium content may be determined by one of the three following methods.

(a) **Colorimetric Determination.**—Fuse the ignited titanium oxide precipitate with 15 to 20 times as much of previously- dehydrated potassium pyrosulfate, $K_2S_2O_7$, which is prepared by heating potassium acid sulfate in a platinum crucible until fumes of sulfuric anhydride are evolved. After fusing, cool the crucible and dissolve the melt in 75 c.c. of cold water and 5 c.c. of concentrated sulfuric acid. If an insoluble residue remains it must

[1] If the concentration of the hydrochloric acid was 6-normal (*i.e.*, d. 1.1), there is little danger of any TiO_2 being precipitated. Care must be taken not to dilute the solution much below this concentration.

be fused again with potassium pyrosulfate. Dilute the solution to 100 c.c. in a calibrated flask and use 50 c.c. or less, according to the titanium content, for the colorimetric comparison.

To prepare a standard solution of titanium, weigh 0.4996 g. of pure anhydrous potassium titanium fluoride, K_2TiF_6, into a platinum crucible. To remove fluorine and form potassium sulfate and titanium sulfate, heat the salt with a little water and concentrated sulfuric acid until fumes are evolved, and repeat the treatment several times. Finally dissolve the titanium sulfate by heating with a little concentrated sulfuric acid and dilute with 5 per cent sulfuric acid to 100 c.c. One cubic centimeter of this solution contains 0.001 g. of titanium. Or, the standard solution may be prepared by fusing 0.1665 g. of pure titanium dioxide with eight times as much sodium carbonate, dissolving the excess sodium carbonate in cold water, filtering and dissolving the residue of sodium acid titanate in 10 c.c. of concentrated sulfuric acid and finally diluting the solution to exactly 100 c.c. at room temperature. One cubic centimeter of standard solution contains 0.001 g. titanium.[1]

Prepare a series of standards by measuring out 1, 3, 5, 10-c.c., etc., portions of the standard titanium solution, diluting each to 50 c.c. in a Nessler tube with 5 per cent sulfuric acid, adding 2 c.c. of hydrogen peroxide (free from fluorine) and mixing. Compare with the standards the color produced with an aliquot part of the solution to be analyzed and 2 c.c. of hydrogen peroxide. The color in the case of dilute solutions may be compared by looking down upon the tubes against a white background. Another method is to place the tube side by side in a colorimeter with a weaker standard and dilute the unknown solution with measured volumes of 5 per cent sulfuric acid, mixing after each addition, until the two solutions are of the same color and dilution. In this case the tubes are held side by side and viewed horizontally. From the known amount of titanium present in the standard it is easy to compute that present in the unknown solution.

[1] The standard solution can be prepared even more easily by digesting 0.1665 g. of pure titanium oxide with 10 c.c. of hot, concentrated sulfuric acid in a porcelain dish. When the oxide has all dissolved, cool and very carefully dilute to exactly 100 c.c. at room temperature. Usually the acid gently ignited to titanium oxide obtained in the analysis can be dissolved by digesting with hot concentrated sulfuric acid.

This colorimetric method is the most satisfactory for the determination of small quantities of titanium. In most cases a satisfactory analysis can be made with a sample of iron or steel weighing only 1 g. The method is not suitable for large amounts of titanium, as the color of the pertitanic acid is best estimated in dilute solutions and when more than 1 per cent of titanium is present a very small aliquot part of the sample has to be taken. The solution should contain at least 5 per cent of sulfuric acid when the test is made and molybdenum, vanadium or chromium must not be present as each of these elements gives a color reaction with hydrogen peroxide. The test is so delicate that one part of titanium can be detected in the presence of one million parts of water.

Computation.—If n_2 c.c. of the standard solution match the color produced with n_1 c.c. of the 100-c.c. solution obtained from s g. of metal, then

$$\frac{10n_2}{s \times n_1} = \text{per cent Ti}$$

Or, if it was necessary to dilute n_1 c.c. of the analyzed solution with t c.c. of 5 per cent sulfuric acid before getting a shade corresponding to n_2 c.c. of standard in 50 c.c. of solution, then

$$\frac{0.2(n_1 + t)n_2}{n_1 \times s} = \text{per cent Ti}$$

(b) Volumetric Determination.—Fuse the impure titanium oxide in a platinum crucible with about ten times its weight of sodium carbonate. Cool, place the crucible in a beaker and cover it with cold water. After all the sodium carbonate has dissolved, filter off the solution from the insoluble sodium acid titanate and ferric oxide and wash the residue with cold water. Allow the funnel to drain completely, pierce the filter with a pointed glass rod, and wash the precipitate into a small Erlenmeyer flask with dilute hydrochloric acid (d. 1.12). Wash the filter with hot hydrochloric acid of the same strength and heat this acid with the residue until all the sodium titanate and ferric oxide have dissolved. Acid more dilute than this will not dissolve the precipitate. If this point is forgotten and water is added, hydrolysis takes place and the titanium is precipitated. Such a precipitate is very hard to filter and wash, so that it is very easy to spoil the analysis at this point.

Concentrate the solution to about 20 c.c. in a 200-c.c. Erlenmeyer flask. Add 10 to 20 c.c. of concentrated hydrochloric acid (d. 1.2) and close the flask with a rubber stopper carrying a Bunsen valve on the outside. To make a Bunsen valve, insert a piece of glass tubing into a one-hole rubber stopper and on the glass tubing place a short piece of rubber tubing sealed at the other end with a piece of stirring rod. Make a slit in the side of the tubing to permit gas to escape from the flask; pressure from the outside squeezes the cut ends of the rubber together so that air from the outside cannot enter the flask. Better still, the flask may be connected, as shown in Fig. 27, with a beaker containing a saturated solution of sodium bicarbonate.[1] Then if there is any back pressure, sodium bicarbonate is sucked into the flask which causes evolution of carbon dioxide and thus prevents air from entering.

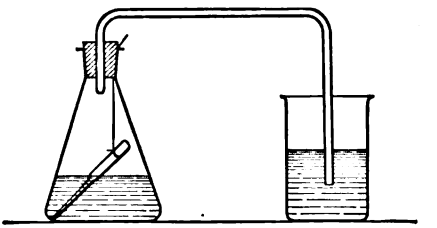


FIG. 27.—Apparatus for reducing titanium solutions.

To reduce the titanium from the quadrivalent to trivalent condition, introduce a piece of 50 per cent zinc-magnesium alloy, weighing about 2 g. or about 3 g. of stick zinc in coarse pieces. It is not necessary that the zinc should be absolutely free from iron. Stopper the flask and allow the reduction to take place for a time in the cold. When the solution has become violet and most of the zinc has dissolved, add 1 or 2 g. more of the metal, in coarse pieces, close the flask quickly, and finish the reduction by heating on the water bath.

During the reduction, the following reaction takes place:

$$2Ti^{++++} + Zn(\text{or } Mg) = 2Ti^{+++} + Zn^{++}(\text{or } Mg^{++})$$

To accomplish the reduction, it is necessary to get all of the quadrivalent titanium into the ionic condition. In attempting to reduce a slightly acid titanium solution, the reduction is usually incomplete on account of hydrolysis even when there is no visible precipitation of titanium dioxide, for the hydrated oxide

[1] A Contat-Göckels valve works very nicely. See *Z. angew. Chem.*, **13**, 620 (1899), or TREADWELL-HALL, "*Analytical Chemistry*" vol. II.

may remain in colloidal solution. In such cases the titration will give too low results. For this reason, it is necessary to have the titanium solution strongly acid to get a complete reduction.

Instead of using a small quantity of zinc and waiting till all has dissolved, a larger piece of metal may be used and suspended in the solution, as shown in the drawing, by means of fine platinum wire. After reducing for three-quarters of an hour to an hour, allow the solution to cool and then remove the excess of zinc, rinsing it with cold water.

Add to the solution 1 or 2 g. of pure ammonium thiocyanate, free from iron, and titrate with ferric chloride solution until a permanent red color, due to ferric thiocyanate, is obtained.

Computation.—If n c.c. of ferric chloride solution, of which 1 c.c. $= t$ g. of titanium, are used in the analysis of a sample weighing s g., then

$$\text{per cent Ti} = 100\, t\frac{n}{s}$$

or, in case the ferric chloride solution was exactly tenth-normal,

$$\text{per cent Ti} = \frac{n}{s}\, 0.481$$

(c) Determination of Iron in Impure Titanium Oxide.—Inasmuch as the impurity present in the ignited precipitate of titanium oxide is chiefly ferric oxide, the quantity of titanium dioxide may be estimated with fair accuracy by determining the amount of iron by titration and then deducting the corresponding amount of ferric oxide from the weight of impure titanium oxide.

The volumetric determination of the iron may be accomplished in the hydrochloric acid solution obtained after fusing the impure titanium oxide with sodium carbonate (p. 236) by the iodometric method described on p. 170, or by the following method, in which tenth-normal permanganate is used..

Titanium is reduced from the quadrivalent to trivalent condition less readily than iron is reduced from the ferric to ferrous state. Thus metallic zinc, which is so often used for reducing ferric solutions previous to titration with permanganate, begins to reduce titanium after the ferric ions are all reduced and the reduction is more or less complete according to the conditions. If the conditions are as described in the previous method, a

quantitative reduction of both iron and titanium takes place. Stannous chloride, recommended on p. 232, also reduces titanium solutions, although it is possible, with a little practice, to reduce the iron and practically no titanium, by stopping the addition of the reagent at the exact point where the solution becomes colorless; further addition of stannous chloride causes the formation of violet, trivalent titanium ions.

Probably the most satisfactory reducing agent, however, for reacting with ferric ions in the presence of titanium is hydrogen sulfide in sulfuric acid solution.

Procedure.—Fuse the impure titanium dioxide with potassium pyrosulfate and dissolve the melt as directed on p. 234. Transfer the solution to a 200-c.c. flask which is fitted with a rubber stopper carrying two glass tubes by which gas can enter and leave the flask. The tubes are each bent once at right angles and the one through which the hydrogen sulfide is to enter reaches nearly to the bottom of the flask, while the other extends just to the lower edge of the rubber stopper. The solution to be reduced should contain about one-tenth its volume of concentrated sulfuric acid. Heat the solution to boiling while passing hydrogen sulfide gas through it. With the small amount of iron present, a few minutes should suffice for the complete reduction of the ferric ions. Continue boiling the solution gently and replace the stream of hydrogen sulfide with one of carbon dioxide and pass this gas through the solution until it ceases to blacken lead acetate paper as it leaves the flask. Cool in a slow stream of carbon dioxide and titrate with potassium permanganate.

Computation.—If p g. of impure TiO_2 were obtained in the analysis of s g. of the original material and the only impurity was ferric oxide which required n c.c. of permanganate which was f-normal, then

$$\text{per cent Ti} = 60.05\,\frac{(p - 0.7985\,n.f)}{s}$$

2. DETERMINATION OF TITANIUM IN INSOLUBLE MATERIALS

(Ferro-titanium and other Titanium Alloys)

Procedure.—Heat 1 to 2 g. of the material which should be pulverized as finely as possible, in a platinum crucible with five

or six times as much of a mixture of 1 part magnesium oxide and 2 parts of anhydrous sodium carbonate (*cf.* p. 125). Mix the sample with the ignition mixture and introduce it into the crucible after first covering the bottom with a layer of the ignition mixture. Carry out the fusion as directed on p. 125.

Transfer the ignited mass to an agate mortar, moisten it with a little cold water and triturate to a paste. Rinse the paste into a beaker using as little water as possible. Add to the contents of the beaker five or six times as much concentrated hydrochloric acid (d. 1.2) as there is water in the beaker, cover with a watch-glass to prevent loss by spattering, and heat gently, stirring from time to time. If the directions are carefully followed, a clear solution will be obtained in a short time.

Concentrate the hydrochloric acid solution, transfer it to a 200 c.c. Erlenmeyer flask, reduce with zinc and titrate as described on p. 237.

If the titanium content is high it may be advisable to use an aliquot part of the solution. In this case do not concentrate the hydrochloric acid solution of the melt, but dilute it with hydrochloric acid (d. 1.12) to 250 c.c. in a calibrated flask and use 100 c.c. for the titration, first concentrating the solution.

In some cases muddy, violet-colored solutions are obtained after the reduction with zinc. This is due to some impurity such as molybdenum or tungsten. In such cases it is advisable to proceed somewhat differently in order to remove the impurities. Extract the product of the first ignition with hot water and wash the insoluble residue of magnesium oxide and sodium acid titanate very thoroughly with hot water. Ignite the filter and its contents in a platinum crucible till the filter is all consumed, mix the residue with three or four times as much sodium carbonate as the original sample weighed, and again heat strongly. Remove the melt from the crucible with the aid of a little cold water, and dissolve in hydrochloric acid as described above.

Test Analyses. (1) *Experiments with Titanium Solutions.* A titanium solution was prepared and titanium dioxide determined by precipitation from acetic acid solution. Duplicate experiments gave 0.0961 and 0.0978 g. TiO_2 corresponding respectively to 0.0577 and 0.0587 g. Ti.

Twenty cubic centimeters of titanium solution were mixed

with 30 c.c. of ferric chloride solution (= 4.8 g. Fe) and the iron removed by the ether separation. The titanium was precipitated from acetic acid solution and the iron titrated by the iodometric method. In one experiment 0.1007 g. of impure TiO_2 were obtained and the iron present required 0.4 c.c. of tenth-normal sodium thiosulfate solution, corresponding to 0.0032 g. Fe_2O_3. The corrected weight of TiO_2 was thus 0.0975 g. corresponding to 0.0586 g. Ti.

In a similar experiment the corresponding values were 0.0993 g. impure TiO_2, 0.2 c.c. sodium thiosulfate = 0.0016 g. Fe_2O_3, 0.977 g. pure TiO_2 and 0.0587 g. Ti.

Twenty cubic centimeters of the titanium solution were titrated with ferric chloride; 1 c.c. of $FeCl_3$ = 0.004912 g. Ti. In duplicate experiments 12.18 and 12.10 c.c. of the ferric chloride solution were used, corresponding to 0.0598 and 0.0594 g. Ti.

Thirty cubic centimeters of titanium solution were mixed with 30 c.c. of ferric chloride solution, the iron was removed by ether, the titanium precipitated as dioxide, and the titanium determined by titration in the hydrochloric acid solution obtained after fusing the impure titanium dioxide with sodium carbonate. In one experiment 12.10 c.c. and in another 12.05 c.c. of ferric chloride solution were required, corresponding to 0.0594 and 0.0592 g. Ti.

Titanium Determinations by Method 2

Duplicate determinations with 2-g. samples of metallic titanium using one-fifth of the solution for the final titration, required respectively 50.5 and 50.7 c.c. of ferric chloride (1 c.c. = 0.004995 g. Ti) corresponding to 63.0 and 63.3 per cent Ti.

With ferro-titanium (Goldschmidt) the values 18.9 and 19.0 per cent Ti were obtained with samples weighing 1 g.

In a sample of cast iron, the titanium was determined gravimetrically, simply purifying the titanium dioxide by heating with sulfuric and hydrofluoric acids to remove silica. The values obtained with 10-g. samples were 0.070 and 0.067 per cent Ti.

Accuracy of the Results and Permissible Deviations

Small quantities of titanium may be separated from iron by the ether process and the titanium precipitated as dioxide. The

volumetric determination of small quantities of titanium is not at all reliable but the results by the colorimetric method are excellent. Results should agree within the following limits:

Per cent Ti	Permissible Deviation
0.05 – 0.2	±0.02 per cent
0.2 – 1.0	±0.03 per cent
1.0 – 5.0	±0.1 per cent
5.0 – 10.0	±0.2 per cent

CHAPTER XVIII

NITROGEN

For many years nitrogen was believed to play an important part in the manufacture of steel. This view, however, has been discredited[1] and the determination of nitrogen is one that is seldom included in the chemical examination of a sample of steel. Yet there is considerable evidence in the literature that the small quantities of nitrogen present in steel, rarely much more than 0.01 per cent, may have considerable influence upon the value of the product. As a rule, nitrogen produces brittleness, but whether this effect is produced by the element alone or only in conjunction with sulfur and phosphorus is not definitely settled. Stromeyer has claimed that nitrogen has ten times more effect than phosphorus in raising the tenacity of steel, and states that in a good specimen of steel the percentage of phosphorus increased by five times the percentage of nitrogen should not exceed 0.080 per cent. Nitrogen is probably present in steel either as Fe_8N_2 or as Fe_4N_2.

1. DETERMINATION OF NITROGEN IN STEEL

METHOD OF A. H. ALLEN[2]

Principle.—When steel is dissolved in sulfuric or hydrochloric acid, all the combined nitrogen is obtained in the form of ammonium salt. If the solution is boiled with an excess of sodium hydroxide, ammonia is distilled off and can be determined by the Nessler test or by absorption in a measured volume of standard acid and titrating the excess of the latter with standard alkali. The quantity of nitrogen present is so small, however, that it

[1] Fay, *Chem. and Met. Eng.*, **24**, 289 (1921) has shown recently that nitrogen causes case hardening and is probably an important factor in cyanide hardening.

[2] First proposed by A. H. Allen (*J. Iron and Steel Institute*, **1879**, 480; **1880**, 181) and modified by J. W. Langley (*cf.* BLAIR'S "*Chemical Analysis of Iron and Steel*").

requires a large sample of steel, 10 g. at least, to give enough ammonia to determine accurately by the latter method.

Reagents Required.—*Distilled Water Free from Ammonia.*—Add a little potassium permanganate and some sodium carbonate to ordinary distilled water and redistil, rejecting the first fourth and last sixth of the distillate.

Standard Ammonium Chloride Solution.—Dissolve 0.0382 g. of pure ammonium chloride in 1 liter of water free from ammonia. One cubic centimeter of this solution is equivalent to 0.01 mg. of nitrogen.

Six-normal Hydrochloric Acid.—Half fill a liter flask with concentrated hydrochloric acid. Through a two-holed rubber stopper, which fits the neck of the flask, insert a dropping funnel and a gas delivery tube connecting the flask with a second flask containing pure water, free from ammonia. Pour some pure, concentrated, sulfuric acid, free from nitrous acid, into the dropping funnel and allow this to flow slowly into the hydrochloric acid, heating the contents of the flask as required. Distil the hydrochloric acid into the pure water until the density of the acid solution thus formed is about 1.1.

Sodium Hydroxide Solution.—Dissolve 300 g. of pure caustic soda in 500 c.c. of water and digest it 24 hr. with a copper-zinc couple. To make the couple, cover about 25 g. of thin sheet zinc with a fairly concentrated copper sulfate solution; after about 10 min. pour off the solution and wash the residue of copper and zinc with cold, distilled water.

Nessler's Reagent.—Dissolve 61.75 g. of pure potassium iodide in 250 c.c. of distilled water and add a cold, saturated solution of mercuric chloride, prepared by obtaining a hot, saturated solution and allowing the excess of the salt to crystallize out on cooling. Add the mercuric chloride solution very carefully, stopping when a slight permanent, red precipitate of mercuric iodide, HgI_2, is formed. Dissolve this by adding 0.75 g. of powdered potassium iodide and then add 150 g. of potassium hydroxide dissolved in 250 c.c. of water. Make up to a liter and allow it to settle over night.

Carefully siphon off the clear solution into a clean bottle and keep it in a dark place. This solution should give the required color within 5 min. Nessler solution contains the complex salt

$K_2[HgI_4]$. The alkaline solution reacts with ammonia, forming a brown precipitate, or a coloration varying with the quantity of ammonia present; the reaction is expressed by the following equation:

$$2K_2[HgI_4] + 3KOH + NH_4OH = O\begin{matrix}\diagup Hg \diagdown \\ \diagdown Hg \diagup\end{matrix}NH_2.I + 3H_2O + 7KI$$

Procedure.—Place 30 c.c. of the sodium hydroxide solution in the 500-c.c. Erlenmeyer flask, *K*, Fig. 28 add 500 c.c. of water and distil until a 50-c.c. portion of the distillate, when treated

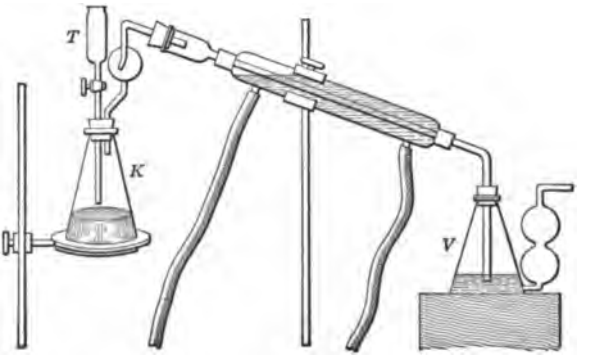


FIG. 28.

with 1 c.c. of Nessler reagent, will give less color than is obtained with 1 c.c. of the standard ammonium chloride solution, diluted to 50 c.c. with water free from ammonia, and similarly treated with Nessler reagent.

Meanwhile dissolve 3 g. of carefully washed steel turnings in 30 c.c. of the pure, 6-normal hydrochloric acid, heating if necessary. Transfer the solution to the bulb of the dropping funnel, *T*, and, when the solution in the flask is boiled free from ammonia, slowly add the ferrous chloride solution. Rotate the contents of the flask to make sure that a good mixture is obtained and then carefully continue the boiling. When about 50 c.c. of distillate is obtained, transfer it to a Nessler tube, which is merely a long, cylindrical tube of uniform bore, mix it with 1 c.c. of Nessler reagent and allow to stand 5 min. Compare the color with

that obtained with 1, 2, 3, etc., c.c. portions of standard ammonium chloride solution, each treated with 1 c.c. of Nessler reagent, diluted to 50 c.c. with best water and allowed to stand 5 min. Hold the tubes side by side in a slightly inclined position and look down upon them with a background of white paper. The standards should be prepared at the same time the test is being made. Make a note of the number of cubic centimeters of ammonium chloride solution required to give the same shade as that of the Nesslerized distillate. Continue to collect portions of the distillate, and match them with the standards, until finally a 50-c.c. portion is obtained which gives a distinctly paler color than that obtained with 1 c.c. of the standard.

Computation.—If n represents the sum of the number of cubic centimeters of standard ammonium chloride solution required to match the various portions of the Nesslerized distillate, in the analysis of a sample of steel weighing s g., then

$$\text{per cent N} = \frac{0.001\ n}{s}$$

2. MODIFICATION OF L. E. BARTON[1]

Dissolve 5 g. of the steel in 40 c.c. of ammonia-free hydrochloric acid and add the solution to the distilling flask exactly as in the above directions. Catch the distillate in a graduated flask and distil until 150 c.c. of distillate are obtained; this will contain all of the nitrogen, as experience has shown.

Then add 25 c.c. of the standard ammonium chloride solution to the contents of the flask and distil into another graduated flask until 150 c.c. of distillate are obtained, which will also contain all of the nitrogen in the standard. To this add 6 c.c. of Nessler reagent. Since the standard solution contains 0.01 mg. per c.c., the standard distillate will now contain $\frac{25 \times 0.01}{156} =$ 0.0016 mg. per c.c. A single standard distillate will serve for the determination of nitrogen in several samples of steel if the comparisons are being made at the same time.

For the color comparison, place 30 c.c. of the distillate from the solution of the steel (= 1 g. of metal) into one of a pair of

[1] *J. Ind. Eng. Chem.*, **6**, 1012 (1914).

Nessler tubes, add 1 c.c. of Nessler reagent and allow the color to develop by letting the solution stand 5 min. Into the other Nessler tube run in the standard distillate until the colors in the two Nessler tubes match, making the final comparison after bringing the solutions to the same volume by the addition of distilled water free from ammonia to one or the other of the tubes. Then the number of cubic centimeters of standard distillate used multiplied by 0.0016 gives the percentage of nitrogen in the steel.

The results in duplicate determinations by this method do not usually differ by more than 0.0005 per cent nitrogen. The average nitrogen content of steel is about 0.004 per cent.

CHAPTER XIX

OXYGEN

Ingot iron, or mild steel, often contains combined oxygen. The amount of oxides present depends upon the extent to which decarburization has been effected by oxidation in the manufacture of the material.

The oxygen is present chiefly as ferrous oxide dissolved in the crystals of ferrite but it may be present as other oxide enclosed in the metal. In 1882 Ledebur[1] proposed a method for the determination of oxygen based upon the reduction of the oxide at a red heat by hydrogen and weighing the water thus formed. Ledebur's method is the one that has been used most for the determination of oxygen in iron and steel but although it reduces quantitatively the oxides of iron, molybdenum, tungsten, etc., to the metallic state, any oxygen combined with manganese, aluminum, silicon, titanium, etc., escapes the determination, or at least for the most part. In 1912, W. H. Walker and W. A. Patrick[2] published a method by which nearly all oxides are reduced. The metal is heated in an electric vacuum furnace with graphite and the carbon monoxide formed is determined.

1. LEDEBUR'S METHOD

To obtain accurate results, it is necessary that the original material be perfectly dry and free from organic matter and that the hydrogen be free from oxygen.

Apparatus.—The hydrogen may be prepared from a Finkener generator,[3] a Kipp generator or by the electrolysis of dilute sul-

[1] *Stahl u. Eisen*, **2**, 193 (1882); Leitfaden für Eisenhütten-Laboratorien, p. 105 (1900).

[2] *J. Ind. Eng. Chem.*, **4**, 799 (1912); *8th Intern. Congr. Appl. Chem.*, **21**, 139 (1912).

[3] Figure 29, at the extreme right.

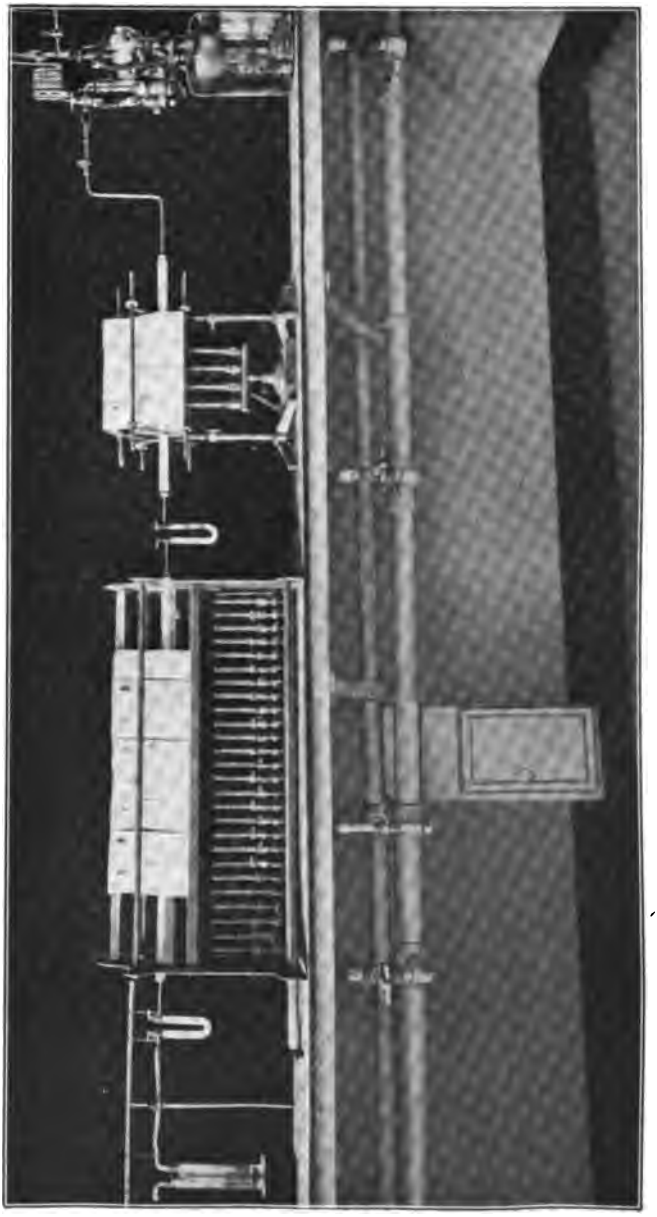


FIG. 29.

furic acid. The gas is washed to remove impurities[1] and then, to remove any possibility of traces of oxygen remaining, it is passed through a hot porcelain tube containing platinized asbestos. The water obtained from the union of hydrogen and oxygen in this tube is removed by passing the gas through a U-tube containing phosphorus pentoxide between plugs of glass wool.

The thoroughly purified and dried gas then enters the porcelain combustion tube in which the sample is to be heated and the water formed from the oxygen in the sample is absorbed in a weighed tube containing phosphorus pentoxide. To prevent contamination of the latter from moisture in the atmosphere, this last absorption tube is connected with a bubble tube containing a little concentrated sulfuric acid; this tube also serves to indicate the rate at which the gas is passing through the apparatus.

Procedure.—Special pains must be taken with the sample to be used in this determination. To remove organic substances such as oil or grease, wash the borings with chloroform, alcohol and ether using reagents which are free from non-volatile residue. Select borings free from rust or scale, unless it is desired to determine the oxygen in such portions of the metal. Finally, dry the sample by heating in a hot closet at 105° and cool in a desiccator.

Before starting the analysis proper, it is necessary to carry out a blank experiment with the apparatus all in place and using the same procedure as in the analysis itself; this is to make sure that there is no gain in weight in the phosphorus pentoxide tube owing to impurities in the hydrogen, to leaky apparatus, or to moisture in the tube.

Pass a current of hydrogen through the entire apparatus without, at first, heating either of the porcelain tubes. After 30 or 45 min. collect a little of the escaping gas in a test tube and test it to see if it will burn quietly. If this is the case, light the burners under the tube containing the platinized asbestos and keep this

[1] In Fig. 29, the purification train consists of a tube containing 50 per cent caustic potash solution (to remove HCl, H_2S, etc.), a tube containing alkaline pyrogallol solution (about 3 per cent pyrogallol in 10 per cent caustic potash: this serves to remove oxygen) and a tube containing concentrated phosphoric acid (to remove most of the moisture).

Instead of pure caustic potash solution, Ledebur recommends a solution of lead oxide in caustic potash.

tube hot as long as a continuous stream of hydrogen is being passed through the apparatus. Detach the phosphorus pentoxide tube, allow it to stand near the balance for 15 min. and weigh. Again connect this tube with the apparatus and heat the empty combustion tube to redness during a period of 30 to 45 min. Then turn out the burners under this tube and allow it to cool while the current of hydrogen is still passing. Detach the absorption tube, allow it to stand at least 15 min. near the balance and again weigh it. If this second weight is within 1 mg. of the first weight, the apparatus is ready for the combustion of the sample.

Weigh out 15 g., or more, of the metal into a porcelain boat. If it is desired to use a larger quantity of the material, weigh it upon a watch-glass, dry in a closet at 105° for an hour, cool in a desiccator, and weigh again. If heating for half an hour longer causes no further loss in weight, introduce the sample into the combustion tube which has already been heated in a current of hydrogen. Large samples may be introduced directly into the combustion tube between plugs of ignited asbestos. Before heating or connecting the absorption tube, pass the hydrogen through the apparatus for an hour in order to remove all traces of atmospheric oxygen. Then connect the weighed absorption tube and begin to heat the tube containing the sample. Gradually raise the temperature till a bright red heat is obtained and keep the tube at this temperature for about 30 min., then turn down the flames and allow the furnace to cool. Finally detach the absorption tube, allow it to stand near the balance for at least 15 min. and weigh.

After the furnace has cooled down with the hydrogen still passing through it, the oxidized sample can be removed from the tube and the apparatus is ready for a new determination.

Computation.—If s represents the weight of sample taken for analysis and p the weight of water obtained in the absorption tube, then

$$\frac{p \times O \times 100}{H_2O \times s} = 88.81\frac{p}{s} = \text{per cent oxygen}$$

Applicability of the Method.—Besides serving for the determination of oxygen in iron, the method can be used with a fair degree of accuracy for determining the extent to which a sample of mate-

rial has rusted and for determining the amount of combined oxygen in samples of metallic tungsten or molybdenum, or in the alloys of these elements with iron.

Test Analyses.—(1) *Determination of Oxygen in Mild Steel.*—Using 40-g. samples the values 0.018 and 0.020 per cent O were obtained in duplicate determinations with one sample and the values 0.016 and 0.015 per cent with another.

2. *Determination of Rust on Cast-iron Borings.*—The borings were composed of coarse particles and of very fine particles. By means of sieves the borings were sorted into three portions according to fineness. Fifteen grams of borings gave 6.795 g. of finest chips, 4.747 g. of coarser chips and 3.456 g. of coarsest chips. Using these proportions of the material the values 2.60 and 2.50 per cent O were obtained by combustion of a 15-g. composite sample.

3. *Determination of the Oxygen Content of Ferro-tungsten.*—Ten-gram portions of the dried and powdered material gave duplicate results of 0.056 and 0.050 per cent O.

4. *Determination of the Oxygen Content of Powdered Tungsten.*—Duplicate determinations with samples weighing about 30 g. gave the values 0.044 and 0.043 per cent O.

5. *Oxygen in Metallic Tungsten and in Metallic Molybdenum.*—The combustion in hydrogen of two different samples of tungsten showed 0.46 and 0.52 per cent O and with two different samples of molybdenum the values 0.22 and 0.59 per cent O were obtained; 10-g. samples were used in each case.

2. METHOD OF WM. H. WALKER AND W. A. PATRICK[1]

Apparatus.—A vacuum furnace of the Arsem type (Fig. 30) having a capacity of about 325 c.c. capacity is recommended.[2] The gun-metal chamber *A* rests inside a water jacket *R*. The cover *B* is fastened to the chamber by means of 18 cap-screws, *D*, and the joint is made tight by a rigid lead gasket. The tube, *J*, through which the furnace is exhausted, is soldered into the cover. The window *G* is fastened by the cover to six cap-screws and the joint is made tight by another lead washer. The mica window *E*

[1] *J. Ind. Eng. Chem.*, **4**, 799 (1912); *8th Intern. Congr. Appl. Chem.*, **21**, 139.

[2] General Electric Co., Schenectady, N. Y., *cf. J. Am. Chem. Soc.*, **28**, 921 (1906).

is placed in the top of the window tube. The brass tubes *W*, through which water flows, serve as electrodes. Between the electrodes the graphite heater *L* is fastened by means of clamps *U*. The crucible containing the substance is supported on the stand shown in the drawing and is thus placed in the hottest part of the furnace.

For evacuating the furnace a small rotary oil pump in series with a Geryk pump[1] works satisfactorily and will give a vacuum

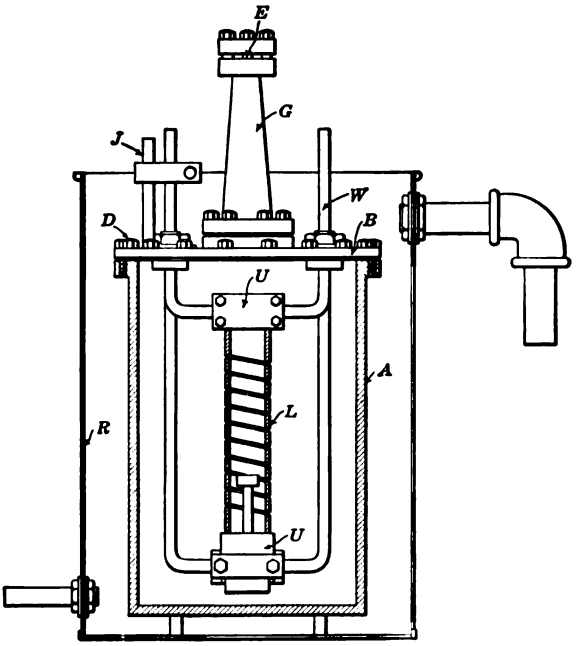


FIG. 30.

of 0.01 mm. in less than 15 min. The apparatus for collecting the carbon monoxide is shown in Fig. 31.

Procedure.—Care should be taken in preparing the sample as described on p. 250. Blank determinations should also be made to determine the quantity of carbon monoxide formed when no oxide is present; and in every analysis allowance must be made for the amount of carbon monoxide thus obtained.

[1] To be obtained from any large dealer in scientific apparatus.

For the analysis itself, weigh 20 to 25 g. of the metal into a small graphite crucible and add 4 or 5 g. of powdered graphite. Place the crucible on the support in the furnace and bolt down the cover of the latter. By means of the vacuum pump, thoroughly exhaust the furnace, then turn on the cooling water and heat the furnace to about 500 to 600° with the pump still running. This is necessary to withdraw the oxygen absorbed by the heater and crucible. As carbon does not begin to reduce oxides below 900° there is no danger in heating the crucible up to 500°. After heating 15 min. at this temperature, allow the crucible

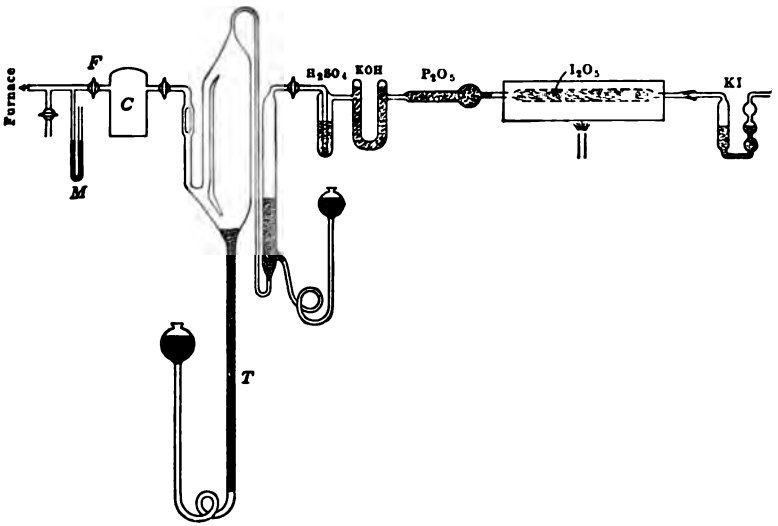


FIG. 31.

to cool, which it does very rapidly. Introduce nitrogen, that has been dried over sulfuric acid and phosphorus pentoxide, into the cold furnace until about half an atmosphere pressure is obtained. Again evacuate the furnace and heat gently as before. Only by such treatment is it possible to reduce the oxygen left in the tube to a reasonably small value.

Now turn off the stopcock leading to the pump and apply 70 volts to the electrodes, which causes a current of about 200 amperes to flow through the heater. A high temperature is obtained very quickly and the metal usually melts within 3 or 4

min. Just as the metal melts violent ebullition often occurs. To stop this open the circuit for a short time and allow the charge to cool somewhat. When the metal is quiet continue the heating for 20 min. Then cool the furnace thoroughly and finally fill the furnace to atmospheric pressure with nitrogen that has been dried over sulfuric acid and phosphorus pentoxide.

The gas now in the furnace is analyzed for carbon monoxide in the following manner:

Exhaust the vessel *C*, Fig. 31, by means of the Toepler pump, *T*, and connect it with the furnace as indicated in the drawing. Open the stopcock at the furnace and note, by means of the differential gage *M*, the difference between the atmospheric pressure and the pressure within the furnace. Open the stopcock *F* and fill *C* and the pump *T* with gas from the furnace. A decrease in pressure corresponding to the volume of gas withdrawn from the furnace is shown by the gage *M*. In this way it is easy to compute, without errors due to temperature variation, what fraction of the original volume of gas in the furnace is used for the analysis.

Slowly force the gas, through the purifying train of concentrated sulfuric acid, solid caustic potash and solid phosphorus pentoxide, into the tube containing iodine pentoxide which is heated to 130°; here the carbon monoxide is oxidized to carbon dioxide and an equivalent quantity of iodine is liberated. The iodine is absorbed in a 10 per cent solution of potassium iodide and finally titrated with $N/100$ sodium thiosulfate solution.

Computation.—If n c.c. of hundredth-normal sodium thiosulfate solution are used in titrating the iodine absorbed in the analysis of a sample weighing s g. and n_1 represents the number of c.c. of the same thiosulfate used in a blank experiment, then

$$N \frac{(n - n_1)\ 0.008}{s} = \text{per cent O}$$

NOTES.—In all cases an appreciable quantity of iodine is obtained in a blank experiment. This is accounted for in three ways: first, a practically constant quantity of iodine is set free when air or nitrogen free from carbon monoxide is led over hot iodine pentoxide; second, there is always a little absorbed oxygen retained on the walls and in the heater of the furnace; third, a trace of moisture is left in the furnace and reacts with the hot carbon. By keeping the temperature of the iodine pentoxide at 130° the oxidation of the carbon monoxide is complete and the decomposition of the

iodine pentoxide is reduced to a minimum. By carefully carrying out the analysis as outlined above, the weight of oxygen corresponding to a blank determination is about 12 mg.

Instead of using the Toepler pump, it is much simpler to use a mercury aspirator, replacing the reservoir *C* (Fig. 31) by a liter bottle which may be filled with mercury. It is then easy to withdraw a known fraction of the furnace contents and to force it through the iodine pentoxide tube.

Although the results obtained by the method are not as accurate as might be desired, and although the method requires a complicated apparatus and careful manipulation, it is nevertheless of value for determining the presence of oxides which are not indicated by the Ledebur method and serves to explain the discrepancies often noted between the oxygen content as determined by that method and the physical and chemical properties of the materials.

TEST ANALYSES

1. OXYGEN FROM FERRIC OXIDE, ALUMINA AND SILICA

To determine the accuracy with which the oxygen of a sample of iron or steel will be converted to carbon monoxide, a number of analyses were made using an iron of very low oxygen content, and adding known quantities of the various oxides in the pure form. In addition to iron oxide, only the very refractory oxides of aluminium and silicon were used; other more easily reducible oxides such as manganese and copper can introduce no difficulties. The weighed amount of pure oxide together with a known weight of iron was placed in the graphite crucible, covered with powdered graphite and heated as described. The following results were obtained:

	Weight of oxide	Oxygen calculated	Oxygen found
Ferric oxide	0.5650	0.1695	0.1700
Ferric oxide	0.6525	0.1960	0.1940
Ferric oxide	0.8400	0.2520	0.2440
Ferric oxide	0.1516	0.0455	0.0480
Alumina	0.4925	0.2310	0.2040
Alumina	0.1860	0.0875	0.0810
Alumina	0.3065	0.1440	0.1260
Silica	0.0673	0.0360	0.0342
Silica	0.0320	0.0181	0.0171

2. COMPARATIVE RESULTS BY THE LEDEBUR AND WALKER-PATRICK METHODS

Sample No. 1 was a special heat of open-hearth steel to which iron ore and an excess of manganese were added in the ladle. The finished steel gave evidence of having a high oxygen content. Number 2 was a high-grade, open-hearth steel. Number 3 was also an open-hearth steel and No. 4 was the same as No. 3 but from an ingot to which ore was added. Numbers 7 and 8 were samples of open-hearth steel and Nos. 9 and 10 were open-hearth iron. Numbers 11*a* and 11*b* were duplicate analyses of an ingot iron of early manufacture and Nos. 12*a* and 12*b* were duplicate analyses of ingot iron of later make.

No.	Per cent C	Per cent Mn	Per cent S	Per cent P	Per cent Si	Per cent Cu	Per cent O, Ledebur	Per cent O, Walker-Patrick
1	0.19	0.92	0.052	0.123	.....	.....	0.006	0.290
2	....	....	.....	.....	.....	.....	0.000	0.090
3	0.17	0.65	0.097	0.064	0.017	.....	.....	0.110
4	0.12	0.17	0.065	0.088	0.015	.....	.....	0.330
5	0.09	0.18	0.061	0.087	0.019	.....	.....	0.310
6	0.14	0.24	0.070	0.092	0.009	.....	.....	0.065
7	0.09	0.33	0.065	0.068	0.006	0.17	0.009	0.021
8	0.08	0.33	0.036	0.070	0.005	0.22	0.010	0.039
9	0.01	0.03	0.050	0.007	0.003	0.20	0.037	0.056
10	0.01	0.04	0.015	0.008	0.004	0.19	0.052	0.064
11*a*	0.01	trace	0.015	0.002	.....	.....	0.069	0.230
11*b*	0.01	trace	0.015	0.002	.....	.....	0.076	0.210
12*a*	0.02	0.03	0.029	0.004	0.0014	0.043	.....	0.100
12*b*	0.02	0.03	0.029	0.004	0.0014	0.043	.....	0.110

CHAPTER XX

ZIRCONIUM

Small quantities of zirconium are sometimes present in steel. Chemists at the Bureau of Standards have studied the various methods which have been proposed for the estimation of zirconium and published a procedure for the determination of silicon, aluminium, titanium and zirconium in the presence of other alloying metals such as possibly tungsten, chromium, vanadium, phosphorus, molybdenum, copper, nickel, uranium and cerium.[1]

Procedure.—Dissolve 5 g. of steel in 50 c.c. of 12-normal hydrochloric acid, heating gently and adding nitric acid in small portions from time to time until the iron is all oxidized to the ferric state.[2] Evaporate the solution to dryness, moisten the residue with 10 c.c. of concentrated hydrochloric acid and repeat the evaporation, this time baking the residue somewhat to decompose any nitrates that may remain. Take up the residue in 50 c.c. of 6-normal hydrochloric acid and heat until all the basic ferric chloride is dissolved. Filter, wash the impure silicic acid with hot 3 per cent hydrochloric acid, and save the filtrate.

Ignite the impure silica and determine its purity by hydrofluoric acid treatment as described on page 118. Fuse the slight residue with a small quantity of potassium pyrosulfate,[3] dissolve the melt in 15 c.c. of 5 per cent sulfuric acid and add this solution to the acid extract from the ether separation, obtained as follows:

Evaporate the filtrate and washings from the silica determination to sirupy consistency, take up in 40 c.c. of 6-normal hydrochloric acid and extract with ether as described on p.

[1] LUNDELL and KNOWLES, *J. I. E. C.*, **12**, 562 (1920).

[2] About 8 c.c. of concentrated nitric acid should be added in 1-c.c. portions.

[3] Potassium acid sulfate fused until all the hydrogen is expelled as water and fumes of sulfuric anhydride begin to escape.

73. The acid extract will contain a little iron and all of the zirconium, titanium, aluminium, manganese, chromium, copper, etc. The ether extract will contain the greater part of the iron and most of the molybdenum; it is discarded.

Boil off the ether in the acid extract, add the sulfuric acid solution obtained in the purification of the silica and a little concentrated nitric acid (about 0.5 c.c.) to make certain that all the iron is in the ferric condition. Dilute to 300 c.c., cool, and precipitate with 20 per cent sodium hydroxide solution, adding 10 c.c. in excess. This serves to precipitate the remainder of the iron together with all the zirconium and titanium. The sodium hydroxide solution should be as pure as possible and free from carbonate. Dissolve the precipitate in hot, 6-normal hydrochloric acid, repeat the sodium hydroxide precipitation and combine the two filtrates and use them for the determination of aluminium. Dissolve the precipitate in hot 6-normal hydrochloric acid and use the resulting solution for the determination of titanium and zirconium. Inasmuch as zirconium phosphate is difficultly soluble in hydrochloric acid, some zirconium may be left on the last filter. To recover it, ignite the filter, fuse the ash with sodium carbonate and dissolve out the sodium salts from the cold melt by treatment with hot water. Discard the aqueous extract and dissolve the residue in hot 6-normal hydrochloric acid, adding the solution to that containing the greater part of the zirconium.

Determination of Aluminium.—(*a*) *In the Absence of Chromium and Uranium.*—Add a few drops of methyl red to the sodium hydroxide solution, neutralize with hydrochloric acid and add in excess 4 c.c. of concentrated hydrochloric acid per 100 c.c. of solution, boil, make barely alkaline with ammonium hydroxide, continue boiling for 3 min. and set aside for 10 min. If no precipitate forms the absence of aluminium is assured. If a precipitate is obtained, filter it off, and discard the filtrate. Without washing the precipitate, dissolve it in hot 6-normal hydrochloric acid, using as little as possible. Dilute to 50 c.c., neutralize with ammonium hydroxide and add 2 c.c. of concentrated nitric acid. Heat to 50° and precipitate phosphorus with ammonium molybdate in the usual manner. Filter and wash with ammonium acid sulfate solution as described on p. 107 and

discard the precipitate. Precipitate the aluminium in the filtrate by ammonium hydroxide as directed above. Filter, and discard the filtrate without washing, dissolve the precipitate in a little hot, 3-normal hydrochloric acid and reprecipitate with ammonium hydroxide. Filter, wash the aluminium hydroxide precipitate a few times with 2 per cent ammonium chloride solution, ignite in a platinum crucible and weigh as Al_2O_3. Inasmuch as this precipitate will always contain a little silica from the action of caustic alkali on glass, it should be treated with sulfuric and hydrofluoric acids to volatilize silicon fluoride and it is advisable to run a blank determination with the same quantities of reagents as used in the regular analysis; when a correction factor is made in this way it is unnecessary to apply the hydrofluoric acid correction provided the alkali solutions do not stand an abnormal time in contact with glass. The silica and alumina content of a solution of sodium hydroxide kept in glass will increase from day to day.

(*b*) *In Steels Containing Chromium.*—Proceed as above until the filtrate from the ammonium phosphomolybdate precipitate is obtained. Then make the solution ammoniacal, oxidize with a little bromine water,[1] make just acid with *nitric acid*, add ammonium hydroxide in slight excess and treat the aluminium hydroxide precipitate as described above.

(*c*) *In Steels Containing Uranium.*—The only modification required is the substitution of ammonium carbonate for ammonium hydroxide as the final precipitant of the aluminium hydroxide.

(*d*) *In Steels Containing Vanadium.*—Aluminium hydroxide, as obtained by the above procedures from steels containing vanadium is contaminated by this element. When dealing with these steels proceed as follows: Fuse the weighed Al_2O_3 residue with potassium pyrosulfate, extract the cooled melt with 5 per cent sulfuric acid, reduce the vanadium in a Jones reductor having ferric alum in the receiver and titrate the reduced solution with standard permanganate. The zinc reduces the vanadium to the bivalent condition and the ferric ions oxidize it back

[1] This oxidation of chromium by bromine in ammoniacal solution is the weak part of the method because the bromine reacts with ammonium ions to form nitrogen and the solution tends to become acid (*cf.* p. 79).

to the quinquevalent state leaving an equivalent quantity of ferrous ions to titrate with permanganate. One cubic centimeter of tenth-normal $KMnO_4 = 0.00607$ g. V_2O_5. Subtract the weight of V_2O_5 from that of the greater impure Al_2O_3 precipitate.

Determination of Zirconium and Titanium.—Dilute the hydrochloric acid solution to 250 c.c., neutralize with ammonium hydroxide so as to leave approximately 5 per cent (by volume) of hydrochloric acid, add 2 g. of tartaric acid, and treat with hydrogen sulfide until the iron has been reduced. Filter if the sulfide group is indicated. Make the hydrogen sulfide solution ammoniacal and continue the addition of the gas for 5 min. Filter carefully and wash with dilute ammonium sulfide-ammonium chloride solution. Filter through a new filter if the presence of iron sulfide in the filtrate is indicated. Save the filtrate.

(The precipitate contains sulfides of iron, manganese nickel and cobalt if these elements are present in the steel. It is preferable to determine these in separate portions of the steel.)

Neutralize the ammonium sulfide filtrate with sulfuric acid, add 30 c.c. in excess and dilute with water to 300 c.c. Digest on the steam bath until sulfur and sulfides have coagulated, filter, wash with 100 c.c. of 10 per cent sulfuric acid, and cool the filtrate in ice water.

Add slowly and with stirring an excess of a cold 6 per cent water solution of cupferron.[1] (The presence of an excess is shown by the appearance of a white cloud which disappears, instead of forming, a permanent coagulated precipitate.) After 10 min. filter on paper, using a cone and very gentle suction, and wash the precipitate thoroughly with cold 10 per cent hydrochloric acid.

Carefully ignite in a tared platinum crucible, completing the ignition over a blast lamp or large Méker burner, cool, and weigh the combined zirconium and titanium oxides ($ZrO_2 + TiO_2$).

Fuse with potassium pyrosulfate, dissolve in 50 c.c. of 10 per cent (by volume) sulfuric acid and determine titanium colorimetrically or volumetrically. Calculate titanium oxide, subtract the weight found from that of the combined oxides, and calculate zirconium.

[1] The ammonium salt of phenyl-nitroso-hydroxylamine.

(c) *Notes on this Method*

1. Phosphorus pentoxide contaminates the precipitate to so slight an extent that it can be disregarded.

2. Vanadium interferes no matter what its valency. The interference is not quantitative. If present in the steel, proceed as usual through the weighing of the cupferron precipitate. Then fuse thoroughly with sodium carbonate, cool, extract with water, filter, and determine the vanadium in the filtrate by adding sulfuric acid, reducing through a Jones reductor into a solution of ferric alum-phosphoric acid (see p. 109) and then titrating with standard permanganate. Vanadium is thus reduced to V_2O_2 and then oxidized to V_2O_5. Calculate to V_2O_5 and subtract from the combined oxides. Ignite in the original crucible the residue insoluble in water, fuse with potassium pyrosulfate and proceed as directed for titanium.

3. Tungsten does not interfere since it is separated from zirconium and titanium by the sodium hydroxide treatment, and from aluminium by the ammonium hydroxide precipitation. If tungsten is present in large amount it may be found desirable to fuse the non-volatile residue from the silicon determination with sodium carbonate, extract with water, filter, dissolve the residue in hot 1 : 1 hydrochloric acid, and add to the acid extract from the ether separation.

4. Uranium is partially carried down when present in the quadrivalent condition, but not at all in the sexivalent state. If this element is suspected, boil out all hydrogen sulfide before the cupferron precipitation, oxidize with permanganate to a faint pink, cool, and proceed with the cupferron precipitation.

5. Thorium and cerium interfere, but they are not thrown down quantitatively. In case these elements are suspected, the oxidized solution used for the titanium determination must be quantitatively preserved and reduced with a little sulfurous acid. The rare earths are then separated by Hillebrand's method[1] as follows: Precipitate the hydroxides with an excess of potassium hydroxide, decant the liquid, wash with water once or twice by decantation and then slightly on the filter. Wash the precipitate from the paper into a small platinum dish, treat

[1] U. S. Geol. Survey, *Bulletin* **700**, 176.

with hydrofluoric acid, and evaporate nearly to dryness. Take up in 5 c.c. of 5 per cent (by volume) hydrofluoric acid. If no precipitate is visible, rare earths are absent. If a precipitate is present, collect it on a small filter held by a perforated platinum or rubber cone and wash it with from 5 to 10 c.c. of the same acid. Wash the crude rare-earth fluorides into a small platinum dish, burn the paper in platinum, add the ash to the fluorides and evaporate to dryness with a little sulfuric acid. Dissolve the sulfates in dilute hydrochloric acid, precipitate the rare-earth hydroxides by ammonia, filter, redissolve in hydrochloric acid, evaporate the solution to dryness and treat the residue with 5 c.c. of boiling-hot, 5 per cent oxalic acid. Filter after 15 min., collect the oxalates on a small filter, wash with not more than 20 c.c. of cold 5 per cent oxalic acid, ignite and weigh as rare-earth oxides which are to be deducted from the weight of the cupferron precipitate.

The above procedure does not give an absolutely quantitative recovery of the rare earths. Experiments indicate a recovery of approximately 85 per cent of the rare earths present in residues containing 100 mg. of zirconia, 2 mg. of thoria, and 2 mg. of ceria.

CHAPTER XXI

ELECTROMETRIC METHODS APPLICABLE TO STEEL ANALYSIS

The electrometric methods to be described here depend upon the measurement of differences in potential or, as in the case of carbon, upon the measurement of electrical resistivity. Although the theoretical principles involved are those of the electrolytic cell and are utilized in electrolytic separations with graded cathode potential, the development of this type of analysis, in which a quantitative estimation of a substance is based wholly upon an electrical measurement, has taken place for the most part since 1900 and such methods have only been applied to the analysis of iron and steel since 1915. For this reason it seems desirable here to discuss the electrolytic theory at some length and without assuming that the reader knows much about electricity or electrical units.

Electricity like all other forms of energy may be resolved into two factors—an intensity factor called *electromotive force* which is measured in *volts* and depends upon a *difference in potential*, and a capacity factor representing the quantity of electricity, which is measured in *coulombs*. It is customary to liken the flow of electricity to that of a body of water; the energy of flowing water depends upon the intensity factor or *head* and upon the quantity of water which flows. The energy in either case is measured by the product of these two factors.

Just as water in flowing has more or less resistance to overcome, so the rate at which electricity flows is determined in part by the resistance to be overcome as well as by the factors of the energy itself.

In 1827, G. S. Ohm enunciated his well-known law: *The strength of current flowing in a conductor is directly proportional to the difference in potential between the ends of the conductor and inversely proportional to the resistance.* If 1 represents the strength

of current, E the electromotive force or difference in potential, and R the resistance, Ohm's law may be formulated,

$$I = \frac{E}{R}$$

The unit for measuring the strength of current is the ampere, that of electromotive force is the volt and that of resistance is the ohm. In terms of these units, Ohm's law reads

$$\text{amperes} = \frac{\text{volts}}{\text{ohms}}$$

The *ohm* is defined as the resistance at 0°C. of a column of mercury 106.3 cm. long and 1 sq. mm. in cross section. The *ampere* is the current that will cause the deposition of 1.1118 mg. of silver in 1 sec. from a solution of silver nitrate. The *volt* is the electromotive force necessary to drive a current of 1 ampere through a resistance of 1 ohm. The *coulomb* is defined as the current corresponding to the flow of 1 ampere in 1 second. The energy of the electric current, or the *power*, is determined by multiplying coulombs × volts. This unit of electricity is often called the *watt-second* but it might just as well be called a *coulomb-volt*. A watt-second is also called a *joule*; it is equivalent to 10 million ergs or to 0.2382 calories of heat energy.

From these elementary units other units such as *milli-ampere*, *milli-volt*, *watt-hour*, *kilowatt-hour* and *kilowatt-year* are derived and have the meanings indicated by their names. Another important unit is the so-called electrochemical equivalent, *Faraday* or *farad*. It signifies 96,500 coulombs or 26.81 ampere-hours and represents the quantity of electricity required to discharge the weight in grams of any univalent ion or radical. Thus if hydrochloric acid is decomposed by electrolysis in such a way that all of the current is used for hydrogen at the cathode and chlorine at the anode, the passage of one Faraday of electricity will cause the discharge of 1 g. of hydrogen and 35.5 g. of chlorine. If 1 gram-molecular weight of hydrochloric acid is completely ionized in aqueous solution, the charges represented as residing upon the hydrogen ions and the chlorine ions correspond to 96,500 coulombs of electricity.

Ions of different metals hold their charges with different degrees of tenacity. Ions with strong electro-affinity are harder

to discharge than those with weak electro-affinity; it requires more voltage to discharge the former although the quantity of electricity involved is determined simply by the valence of the ion. If a free element is placed in contact with the ions of a metal of weaker electro-affinity, the charge on the latter passes to the former; thus placing zinc in copper sulfate solution causes zinc to dissolve and copper to precipitate,

$$Cu^{++} + Zn \rightarrow Cu + Zn^{++} \qquad (1)$$

This is known to all chemists but often too little emphasis is placed upon the fact that reactions of this type are to some extent reversible. The more copper ions and the fewer zinc ions present, the easier it is for the copper to be deposited and for the zinc to dissolve. As the reaction progresses it slows down, although in this particular case the reaction appears to take place until all the copper is precipitated because there is so much difference in the electro-affinities of these two metals.

The elements, especially the metals, are often classified with respect to their electrochemical affinities. The more common metals are arranged in the following order: K, Na, Be, Sr, Ca, Mg, Al, Cr, Mn, Zn, Cd, Fd, Co, Ni, Sn, Pb, H, Sb, Bi, As, Cu, Hg, Ag, Pt, Au. In general, a metal placed in contact with ions of a metal which comes after it in this series will dissolve and the original ions will be precipitated as free metal; there are many apparent exceptions to this rule because other factors other than relative electro-affinities come into consideration.

The tendency for zinc to dissolve when placed in copper sulfate solution is often explained by saying that zinc has a greater *electrolytic solution pressure* than copper. This electrolytic solution pressure, or tendency of the metal to pass into solution as positively charged ions, cannot be measured directly but its theoretical value can be computed. The table of electro-affinities is often called the table of electrolytic solution tensions. In other words, electro-affinity and electrolytic solution tension are equivalent theoretical forces used to explain the same phenomena; the element which has the greatest solution tension naturally is the one which holds on to the electric charge with greatest tenacity after the ions are once formed.

Again, if we define oxidation as the process of adding positive

charges or removing negative charges from a metal or ion, it is clear that in equation (1) zinc is oxidized and copper is reduced and another way of explaining the reaction is to say that zinc has a greater *reduction potential* than copper. The electro-chemical series, therefore, may also be called the series of *normal reduction potentials* or, more briefly, the *voltage series of the elements.* Moreover, the tendency of *any* equation of oxidation and reduction reaction to take place may be measured in terms of voltage and the ions concerned may be assigned a place in the table; for example, the tendency of ferrous ions to become ferric ions is about the same as that of metallic copper to form cupric ions and zinc will reduce ferric ions just about as readily as it will precipitate copper.

When zinc is placed in copper sulfate solution, equation (1), it is clear that a flow of electricity takes place and it is possible to utilize this current as in the Daniell cell in which a strip of zinc is placed in zinc sulfate solution and a strip of copper is placed in copper sulfate solutions; the two metals are connected externally with a wire and the two solutions are in electrical contact, being separated only in some such way as by a porous wall which serves to hinder diffusion. If the copper sulfate solution is kept away from the strip of zinc, no chemical reaction takes place until the two metals are connected by the wire. The conventional way of expressing the flow of current in this cell is as follows:

$$\underset{\longleftarrow}{\overset{\text{In the external circuit}}{}}$$

$$\mathrm{Zn/ZnSO_4/CuSO_4/Cu}$$

$$\underset{\longrightarrow}{}$$

In the solution

The arrow shows the positive to negative direction of the current.[1]

[1] The modern electron theory is based on the assumption that the flow of electricity is really due to the movement of negatively-charged electrons so that the current really flows in the negative to positive direction. The chemist sometimes thinks of the positively-charged ions passing from the zinc to the copper *in the solution* but the physicist thinks first of the positive charges passing from the copper to the zinc *on the wire.* The chemist thinks of zinc as positive because it forms ions with a positive charge; the physicist remembers that the metal is left negative when the solution becomes positive. Both points of view are correct but are confusing to the beginner.

When zinc dissolves in the Daniell cell it has to overcome a certain resistance which increases with the concentration of the zinc ions already in solution; the pressure exerted by dissolved ions is called *osmotic pressure* and tends to neutralize the electrolytic solution pressure. Nernst, with the aid of integral calculus, has computed the electromotive force, E, which results when a metal of P electrolytic solution pressure is placed in contact with a solution of its own ions having the osmotic pressure P. If R represents the gas constant of the well-known expression $pv=n\mathrm{RT}$ expressed here in volts $\times$ coulombs, T the absolute temperature, F the electrochemical equivalent, and n the valence of the ions, the Nernst formula reads:

$$\mathrm{E} = \frac{RT}{nF} \log_e \frac{P}{p}. \qquad (2)$$

It is important to note that the observed electromotive force, or voltage E, varies with the temperature, concentration of the solution (which determines the osmotic pressure), and with the valence of the ions. R, the gas constant, has the value 8.316 when expressed in watt-seconds and F represents 96,500 coulombs. P, however, is a specific property of the metal in question and does not vary. If the value of p is kept the same for a series of metals of the same valence n, it is obvious that the observed values of E will be proportional to the values of P for the different metals. The tendency of one metal to precipitate another depends upon the values of E under the conditions in question, and it is often true that with metals A and B the value of E_A is greater than E_B when P_B is larger than P_A and this is why a metal will not always precipitate another metal that follows it in electrochemical series; it will do so if the values for p are equal.

To precipitate a metal at the cathode by means of the electric current, it is necessary to overcome the electromotive force E, or oxidation potential, and the so-called *decomposition-potential* is reached as soon as the value of E is exceeded. It follows from the Nernst formula that the decomposition voltages increase as the solution becomes more dilute and this is a well-known fact.

If we substitute the values for F and R in the formula, assume that the measurements are made at a laboratory temperature of

18°C. and divide by 0.4343 to change natural logarithms to common logarithms, equation (2) becomes

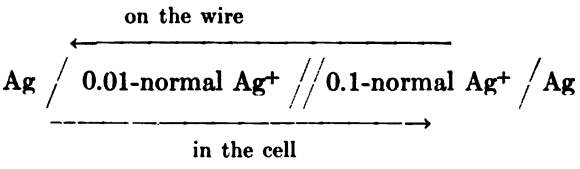
$$E = \frac{0.058}{n} \log \frac{P}{p} \qquad (3)$$

If the following metals are placed in *normal* solutions of their soluble and highly ionized salts and the resulting potential differences measured against a normal hydrogen electrode as arbitrary zero, the values will be approximately: K = 2.93, Na = 2.72, Ba = 2.8, Ca = 2.6, Mg = 1.5, Mn = 1.08, Zn = 0.77, Fe = 0.43, Pb = 0.12, H = +0.0, Cu = −0.34, Ag = −0.8, Hg = −0.86, Au = −1.5.

The positive charge in this table signifies that the current flows in the solution from the metal to the hydrogen electrode and on the wire from the hydrogen electrode to the metal back to the starting point; the metal itself is negative to the solution and, for this reason, many authorities substitute − signs wherever + signs are used in the above table and + signs for the − signs. It will be noticed that the magnitude of the observed values does not follow exactly the same order as that of the electrochemical series and this is due to the fact that the osmotic pressure of the ions in a normal solution of a bivalent metal is only about half as large as that of a normal solution of a univalent metal. Thus the values for barium and calcium are near that of sodium, whereas if solutions were used containing *molal* concentrations of the ions, the values for barium and calcium would be much lower than that of sodium.

The Nernst formula as expressed in equation (3) shows that when a metal is in contact with its ions, the observed values of E will fall 0.058 volt for each tenfold increase in the osmotic pressure of the ions of a univalent metal, 0.029 volt for each tenfold increase in the osmotic pressure of the ions of a bivalent metal and 0.019 volt for a corresponding increase in concentration of trivalent metal ions. In the Daniell cell, the electromotive force will be 1.11 volts if the copper sulfate and zinc sulfate are each of normal concentration. As the cell is used the concentration of the zinc ions increases and that of copper ions diminishes, but the concentration of the latter would have to be about 10^{-37} normal before there would be as much tendency for copper to dissolve as for zinc.

A galvanic cell similar to the Daniell cell can be made with many other pairs of metals and the farther apart the elements are in the electrochemical series, the greater will be the voltage of the cell. Since the potential of a metal against a solution varies with the concentration of the latter it is evident that silver immersed in 0.1-normal silver nitrate solution will have less tendency to dissolve than silver immersed in 0.01-normal silver nitrate solution. A so-called *concentration cell* may be constructed in which the positive to negative direction may be represented as follows:



The actual voltage of such a cell has been found to be 0.055 volt which is near the theoretical value 0.058 which the Nernst rule indicates would be found if the 0.1-normal solution yielded exactly ten times as many ions as the 0.01-normal solution and if there were no differences in potential at any other part of the circuit.

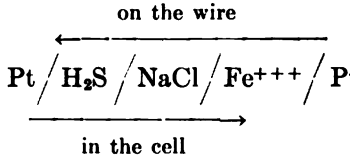
The Nernst formula applied to concentration cells is

$$E_{18} = \frac{0.058}{n} \log \frac{c_1}{c_2} \qquad (4)$$

in which E and n have the usual meaning and c_1 and c_2 represent the concentration of the ions at the two electrodes.

The Daniell cell depends upon the *oxidation* of zinc and the *reduction* of copper. A cell can be constructed from substances involved in any reaction of oxidation and reduction. Thus a cell can be constructed on the basis of the reduction of ferric ions by means of hydrogen sulfide and the reaction will take place without any of the hydrogen sulfide coming in contact with any of the ferric salt if suitable electrical contact is provided. To make such a cell, place a platinum electrode in a beaker containing ferric chloride solution and connect this electrode by means of a wire with another platinum electrode immersed in sodium chloride solution. Connect the two solutions also by

means of a *salt bridge;* this may take the form of an inverted U-tube filled with salt solution. Now pour hydrogen sulfide water into the beaker containing the sodium chloride solution. The hydrogen sulfide will be reduced to sulfur and hydrogen ions will be formed in one beaker; the ferric ions will be reduced to ferrous ions in the other beaker and the direction of the current is indicated by the following diagram:



Some of the most important electrometric methods are based upon potential measurements which indicate the concentration of hydrogen ion in a solution.

Water ionizes slightly into hydrogen and hydroxyl ions:

$$H_2O \rightarrow H^+ + OH^- \qquad (5)$$

The mass action law applied to this ionization reaction is

$$\frac{(\text{conc. } H^+) \times (\text{conc. } OH^-)}{(\text{conc. } H_2O)} = \text{a constant.}$$

In a sample of pure water at 18°, the concentration of the hydrogen ion expressed in moles per liter is about 10^{-7} and in these units the concentration of the hydroxyl ion is the same.

Now in reaction (5) the concentration of the water is not changed appreciably by any changes of ionization that may take place in dilute solution, so that from equation (5) we may say (conc. H^+) × (conc. OH^-) = 10^{-14} for any solution at 18°. If a hydrogen electrode is placed in a solution together with a standard electrode of known electromotive force, the measurement of the difference in potential between the two electrodes will indicate the concentration of the hydrogen ions in the solution. Besides determining the actual hydrogen ion concentration, the neutralization of an acid by a base can be followed even in solutions which are highly colored and the exact neutral point can be determined in many cases more accurately than it is possible to titrate by means of the usual indicators in a perfectly clear solution.

The potential of the normal hydrogen electrode is 0.28 volt below the absolute zero potential at 25°. That of the calomel electrode is –0.28 volt referred to a normal hydrogen electrode or –0.56 volt on the absolute scale at 25°C. when normal KCl is used as electrolyte.

Hildebrand[1] used an apparatus for electrometric titration which is illustrated by the diagram shown in Fig. 32.[2] The beaker in which the titration is made contains the hydrogen electrode, *h*, and the calomel electrode, *C*. The former consists of an S-shaped platinum electrode covered with platinum black and kept saturated with hydrogen gas, H_2, introduced through the side arm of an enveloping tube. The calomel electrode is connected through the switch *K* with the galvanometer *G* and thence to the positive pole of the battery *B*. By means of the sliding contact *S* a variable fraction of the current from the battery passes through the galvanometer to the calomel electrode opposing the current which arises from the difference in potential between the electrodes dipping in the titrated solution. By pressing the key, *K*, and moving the sliding contact until the galvanometer needle shows no current, the voltmeter *V* gives the potential of the current which corresponds exactly to that between the two electrodes. This method gives an accuracy of 1 or 2 per cent in the determination of the electromotive force and this gives satisfactory results in many titrations. An accuracy of about 0.03 per cent in the voltage measurement can be obtained by using a potentiometer, such as type *K* of the Leeds and Northrup Company.

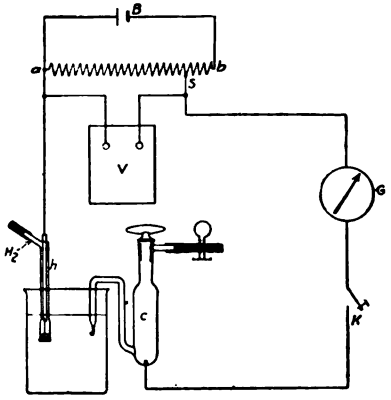


FIG. 32.

In oxidimetric titrations, which are of special interest in the

[1] *J. Am. Chem. Soc.*, **35**, 847 (1913).

[2] Reproduced by permission from the catalog of A. H. Thomas Co.

analysis of iron and steel, the method of procedure is similar except that a polished platinum electrode, exposing as little surface as possible to the solution, is substituted for the hydrogen electrode and the calomel electrode is connected to the negative pole of the battery *B*. Palladium is unsuitable as an electrode, probably because of its tendency to occlude hydrogen, and pure gold is better than an alloy of gold and palladium, but even gold is inferior to polished platinum. Poor results are likely to be obtained with a dirty electrode. An electrode should be cleaned before using it by treatment with acid followed by gentle ignition and should be kept under hydrochloric acid between titrations.

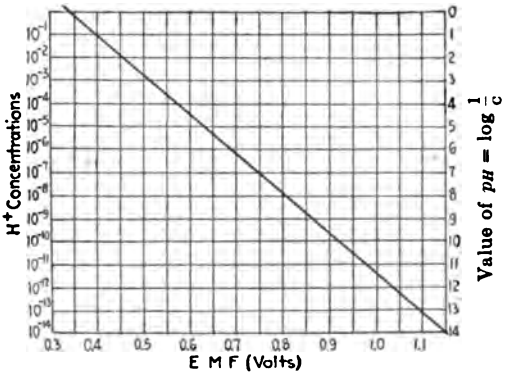


FIG. 33.

For the most accurate results in electrometric titrations, whether acidimetric or oxidimetric, the titrated solution should be stirred mechanically and the potentials observed during the titration should be plotted against the volumes of standard solution added. For most oxidimetric titrations, however, it is not at all necessary to know the exact value of the potential. During the progress of the titration, a slow change in voltage takes place but at the end-point there is almost always a sudden change.

Figure 33 shows the relation between measured potential differences of a hydrogen electrode in solutions of varying degrees of acidity compared with the normal hydrogen electrode. If the concentration of H^+ is designated as c, formula (4) on p. 270 becomes

$$E_{18} = 0.058 \log \frac{1}{c}$$

To compute the actual H concentration from the observed voltage the value of $\log \frac{1}{c}$ is obtained first and Sörensen has suggested that this value be called the p_H of the solution in question, or the hydrogen ion exponent. In Fig. 33 the values given on the left represent the actual concentration of H^+ and the values on the right are those of p_H.

Figure 34 shows independent curves obtained by Hildebrand

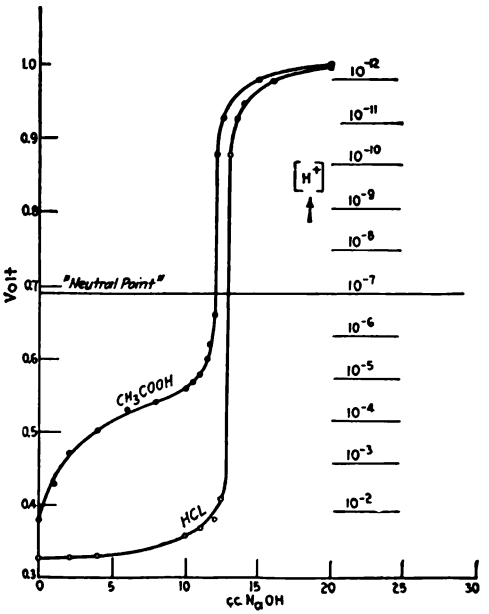


FIG. 34.

in the titration of acetic and hydrochloric acids using a hydrogen electrode against a calomel electrode. At the neutral point, the concentration of H^+ is 10^{-7} as in pure water. In the case of acetic acid, the curve shows that it is a weak acid and that normal sodium acetate is easily hydrolyzed and gives an alkaline reaction.

Soon after the publication of Hildebrand's paper, Forbes and Bartlett[1] published a method of titrating ferrous salts by dichro-

[1] *J. Am. Chem. Soc.*, **35**, 1527 (1913). Crotagno in 1900 had proposed using electrometric titrations for oxidimetric methods of analysis.

mate with a somewhat simpler apparatus. Instead of the voltmeter and rheostat, a thin wire of manganin, German silver or nichrome was stretched over a strip of wood and provided with a sliding contact. During the progress of the reaction, the sliding contact was moved so that the galvanometer needle showed little if any deflection but on reaching the end-point, one drop of dichromate sent the galvanometer needle off the scale.

Roberts and Hostetter[1] have shown how a few tenths of a

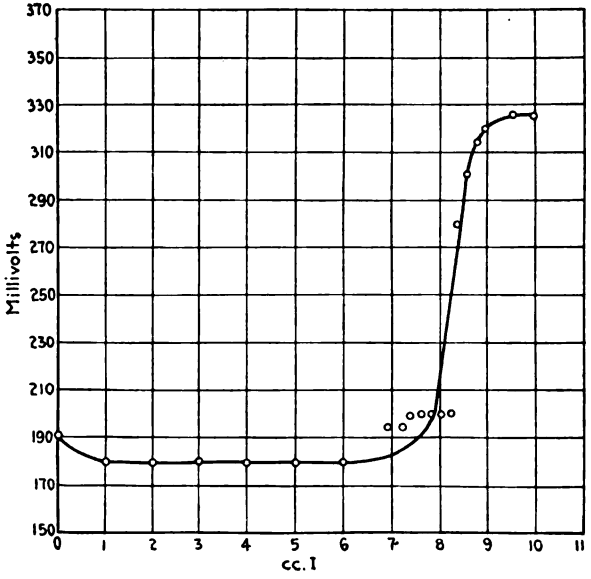


FIG. 35.

milligram of tin, chromium, ferrous or ferric iron can be determined with accuracy by a simple electrometric titration, and Roberts[2] has shown how a sensitive potentiometer can be made at a relatively low cost.

Figure 35 shows results obtained by Robinson and Winter[3] in the electrometric titration of the arsenite in a sample of London purple with tenth-normal iodine.

[1] *J. Am. Chem. Soc.*, **41**, 1337 (1919).
[2] *Ibid.*, **41**, 1358 (1919).
[3] *J. Ind. Eng. Chem.*, **12**, 775 (1920).

Figure 36 shows results obtained by Roberts and Hostetter in titrating iron. These curves are selected at random merely to give an idea of the sudden change in oxidation potential that takes place at the end-point of the reaction.

Several electrometric methods which have been found successful in busy testing laboratories have been proposed by G. L. Kelley[1] and his co-workers of the Midvale Steel Company and they have devised, with the aid of Leeds and Northrup, a special apparatus for these electrometric titrations. Two views of this apparatus[2] are shown in Figs. 37 and 38.

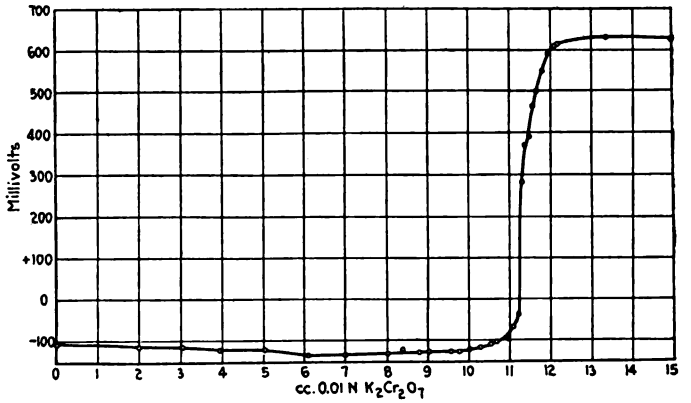


FIG. 36.

The apparatus consists essentially of a wooden case with an upright carrying the motor, burettes and electrodes. In the case are two dry cells, an adjustable resistance, and a reflecting galvanometer. On the upper surface of the case is a ground glass scale on which the light from the galvanometer is thrown. A knurled head inside of the case permits of adjusting the zero point of the galvanometer and another on the side controls the resistance.

The standard carries the burettes, the electrodes, and the motor for driving the stirrer. In addition, provision has been

[1] *J. Ind. Eng. Chem.*, **9**, 780 (1917). Other references are given at the end of this chapter.

[2] These illustrations are reproduced from the catalog of A. H. Thomas Co. (1920).

made for a reservoir of the electrolyte which is used in the calomel cell. This makes possible, without change in its potential, the displacement of the impure electrolyte which may have accumulated in the tip of the electrode. A pan on an adjustable support, specially treated to resist acids, carries the beaker in which the

FIG. 37.

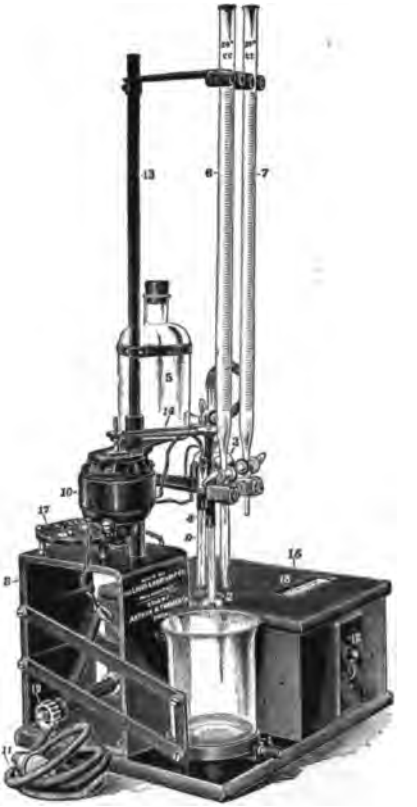


FIG. 38.

titration is made. Two switches are mounted on the sides of the case, one of which controls the galvanometer light and motor, while the other closes the potentiometer circuit.

To operate the instrument, a beaker containing the solution to be analyzed is placed on the pan and the support raised and locked in position. The switch controlling the galvanometer

light and motor is then closed. The other switch closes the potentiometer circuit and a slight turn of the knob controlling the resistance is sufficient to bring the beam of light on the scale. In titrating a series of solutions, this latter adjustment need be made only once. During the operation, which is quick, certain and convenient, the analyst watches the beam of light until a permanent change of potential is noted. In general, the first permanent large change marks the end-point of the reaction.

A rheostat for varying the speed of the motor stirrer is mounted on a casting attached to the box.

Description of Components

Calomel Electrode Cell (Fig. 39).—The calomel electrode rests in a metal collar attached to the upright at *E*. The glass stopcock at *B* allows liquid to flow into the cell from the reservoir to which it is connected by rubber tubing at *A*. When this stopcock is opened, the capillary tube at *D* is flushed, thus insuring the purity of the electrolyte in the cell. The cell may be filled through the opening at *C*, which is then closed. A platinum-tipped wire at *F* makes contact with the external circuit. The capacity of the cell is about 100 c.c. A small amount of mercury is placed in the bottom of the cell and covered with Hg_2Cl_2. The cell is then filled with the neutral liquid, a normal solution of KCl. This gives a constant potential difference of about 0.56 volt between the Hg and the solution, the Hg being + to the solution.

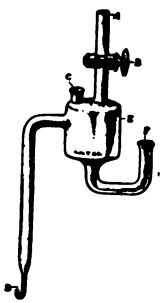


Fig. 39.

Potentiometer.—The e.m.f. of the electrolytic cell is balanced against the fall of potential across a slide wire in circuit with two dry cells and a resistance. The total resistance of the slide wire is about 50 ohms. This resistance can be varied, to secure a balance, by means of a knurled head on the outside of the case.

Galvanometer.—A Leeds and Northrup Company Reflecting Galvanometer is used with this outfit. This instrument is sufficiently sensitive for the purpose and has the further advantage of a very short period. It is rugged in construction and will withstand as much rough usage as an ordinary voltmeter. The image of the lamp filament is reflected to a translucent scale which is placed on the top of the box. This places the scale where it can most easily be seen by the operator while titrating. The lamp furnished with this instrument has a single straight filament of high brilliancy.

Heating Unit.—A heating unit is mounted on a socket on the inside of the box for the purpose of keeping the galvanometer circuit dry at all times and preventing possible "leakage" due to moisture.

Motor and Stirrer.—The stirrer consists of a three-bladed glass propeller cemented into a brass rod and belted to a small electric motor. This motor is securely attached to the upright and is equipped with a rheostat for variable speeds.

Reservoir.—The reservoir consists of an aspirator bottle, 500 c.c. capacity, firmly attached to the upright.

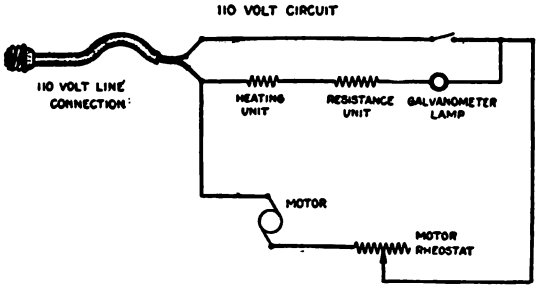


FIG. 40.

Switches and Connections(Fig. 40).—Two switches are mounted on the box; one controls the motor and galvanometer light, and the other throws in the potentiometer circuit (see Fig. 41). All connections, except to dry cells, are soldered and the insulation is designed to prevent all possible "leaks." All metal parts are treated with a special acid-resisting varnish. The measuring circuit is carefully insulated from the motor circuit.

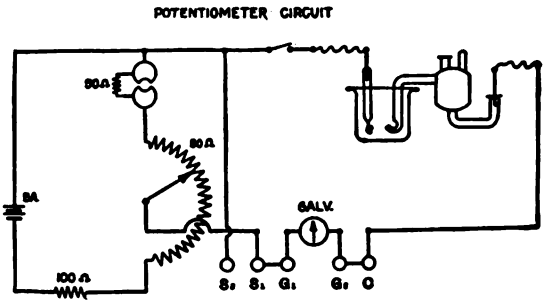


FIG. 41.

The numbers in Figs. 37 and 38 refer to the following parts 1, beaker support; 2, stirrer propeller; 3 calomel electrode cell; 4, stirrer shaft; 5, reservoir for solution used in the calomel cell; 6 and 7, burettes; 8, metal frame; 9, platinum electrode tube; 10, stirring motor; 11, flexible cord and plug; 12, push button switch; 13, upright support; 14, coil spring belt for fastening stirrer; 15, potentiometer box; 16, galvanometer switch; 17, rheostat for varying speed of stirrer; 18, ground glass scale for showing position of light from the galvanometer mirror.

1. ELECTROMETRIC DETERMINATION OF CHROMIUM IN STEEL[1]

Principle.—The steel is dissolved in sulfuric acid, carbides are decomposed by evaporating and the ferrous iron is oxidized by means of nitric acid. By ammonium persulfate in the presence of silver ions, the chromic ions are oxidized to chromic acid. The excess of persulfate is destroyed by boiling and any permanganate is reduced by the careful addition of hydrochloric acid. The cold solution is then titrated with freshly-standardized ferrous sulfate solution, using the electrometric apparatus for determining the end-point.

$$Cr + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2 \uparrow \text{ (solution in acid)}$$

$$2Cr^{+++} + 3S_2O_8^{=} + 6H_2O \rightarrow 2CrO_3 + 6SO_4^{=} + 12H^+ \text{ (with } Ag^+ \text{ as catalyzer)}$$

$$CrO_3 + 3Fe^{++} + 6H^+ \rightarrow Cr^{+++} + 3Fe^{+++} + 3H_2O$$

Solutions Required.—1. *Sulfuric Acid* (d. 1.2).—Pour concentrated sulfuric acid into five times as much water; the diluted acid is approximately 6-normal.

2. *Silver Nitrate Solution.*—Dissolve 2.5 g. of solid in 1 liter of water; this solution is approximately 0.015-normal.

3. *Potassium Dichromate.* Dissolve 2.83 g. of pure dichromate crystals and 5 g. of sodium carbonate in enough water to make exactly 1 liter; this solution is 0.0577-normal and 1 c.c. = 0.001 g. of chromium. Commercial dichromate should be recrystallized and dried at 150° for several hours.

4. *Ferrous Sulfate Solution.*—Mix 23 g. of pure ferrous ammonium sulfate with 50 c.c. of concentrated sulfuric acid and dilute slowly with water. When cold, dilute to exactly 1 liter. This solution is 0.0587-normal when freshly prepared. The solution is intentionally made a little stronger than the dichromate solution because it gradually oxidizes on standing and becomes weaker as a reducing agent. In a busy laboratory it is often convenient to have the two solutions of exactly the same strength and this can be done each day by diluting enough of the ferrous sulfate solution for the day's use as determined by daily standardization of the solution.

[1] KELLEY and Others: *J. Ind. Eng. Chem.*, **8**, 722 (1916); **9**, 632, 780 (1917).

For steel analysis, it is safe to depend upon the purity of recrystallized potassium dichromate provided a fresh solution is made up each week. The strength of the ferrous sulfate solution must be checked daily. It can be titrated against the dichromate solution electrometrically.

If it is desired to check the value of the potassium dichromate solution, a convenient method is to titrate the ferrous sulfate solution against permanganate which has been standardized against sodium oxalate (p. 62) and then titrate the ferrous sulfate against dichromate in the electrometric apparatus.

Procedure.—Dissolve 1 g. of the steel in 70 c.c. of sulfuric acid (d. 1.2). If, however, less than 0.5 per cent of chromium is likely to be present, use twice as much sample and not over 100 c.c. of acid and if more than 5 per cent of chromium is present, use correspondingly less steel without changing the volume of sulfuric acid. Samples need not be weighed closer than to the nearest milligram.

If carbides are left unattacked, as shown by a turbidity and sometimes by dark particles, evaporate the solution until salts begin to crystallize.[1] Dilute carefully with water to 50 c.c., heat to boiling and oxidize the iron by adding about 2 c.c. of concentrated nitric acid, drop by drop. The nitric acid is added until the dark-brown color of $FeSO_4.xNO$ disappears. Boil the solution about 5 min. to expel oxides of nitrogen. Dilute with hot water to a volume of 250 to 300 c.c., add 10 c.c. of silver nitrate solution and 20 c.c. of ammonium persulfate solution. Do not add these solutions in the reverse order, as in the absence of silver ions the oxidation of chromium and manganese does not take place in the desired manner. When manganese is present, permanganic acid is formed. Boil the solution vigorously for 10 min. If the solution contains chlorides which would interfere with the reaction, this is shown by the formation of silver chloride precipitate. If the oxidation of the chromium is incomplete, the red color of the permanganate will not appear from the manganese in the steel. In that case add more silver nitrate and a

[1] If this method fails to decompose carbides, dissolve another sample in 60 c.c. of 6-normal hydrochloric acid, add nitric acid to oxidize the iron and evaporate to fumes in order to remove all hydrochloric acid. The treatment to destroy carbides appears to be unnecessary with tungsten steels.

fresh portion of ammonium persulfate. While the solution is still boiling add 5 c.c. of 3-normal hydrochloric acid to decompose the permanganate into soluble manganous salt and boil at least 5 min. longer to remove any chlorine formed and to make sure that the persulfate is all decomposed. Cool to about 20° and titrate electrometrically.

In titrating, first bring the beam of light near the left end of the scale. Add standard ferrous sulfate slowly until the beam of light has been moved permanently toward the right. Then add standard potassium dichromate until the light will move no farther toward the left and finish the titration by adding ferrous sulfate carefully until a small permanent displacement is again obtained.

Computation.—If the concentration of the potassium dichromate and ferrous ammonium sulfate solutions is adjusted so that 1 c.c. of each is equivalent to 1 mg. of chromium, the per cent of chromium in a sample of steel weighing 1 g. is found by subtracting the volume of potassium dichromate solution used from the total volume of ferrous ammonium sulfate and moving the decimal point one place to the left.

In general, if s represents the weight of sample, N the normality of the potassium dichromate solution and f the value of 1 c.c. of ferrous ammonium sulfate in terms of the potassium dichromate solution, then, when a c.c. of ferrous solution and b c.c. of dichromate,

$$\frac{(a \times f - b)\, N \times 0.01733 \times 100}{s} = \text{per cent Cr}$$

NOTES.—In titrating sodium oxalate with potassium permanganate there is no advantage in using the electrometric apparatus but with it better results are obtained than by other methods in titrating (1) permanganate and ferrous sulfate, (2) chromate and ferrous sulate sulfate and (3) chromate + excess ferrous sulfate + permanganate + ferrous sulfate to end-point. In titrating a chromate solution, the addition of ferrous ions usually causes at first an anomalous rise but with permanganate solution this anomaly does not appear with the same regularity and is less marked. In titrating dichromate with ferrous sulfate, the change in potential is always abrupt when the end-point is reached but with permanganate and ferrous sulfate the end-point is not so sharp; it is advisable, therefore, to add ferrous sulfate in excess until a marked change in potential takes place, then add permanganate until the original potential is reached or until 2 or 3 drops produce no

further change and then finish with ferrous sulfate solution. Probably during the first addition of ferrous sulfate to permanganate some colloidal manganese dioxide is formed which requires an excess of ferrous sulfate to decompose it. In the final stage this manganese dioxide suspension is not formed and a sharper end-point results.

If vanadium is present it will be titrated. In this event use the end-point described in the vanadium determination. The chromium may be calculated as follows: Multiply the vanadium titration as found in a separate determination of vanadium by 0.339, which gives the amount to be subtracted from the titration of chromium and vanadium together.

Tungsten does not interfere with this determination if the volume of the solution is not too great at the time of oxidation with nitric acid. Tungstic acid does not occlude chromium, although it does occlude vanadium. When chromium and vanadium are oxidized together by ammonium persulfate and silver nitrate, the oxidation of chromium is complete, and of the vanadium only that part which is retained by the WO_3 remains unoxidized.

If the end-point obtained on titrating is not sharp, 25 c.c. of sulfuric acid (d. 1.58) may be added. Results by this method are said to be excellent, and remarkably concordant values are obtained with low chromium content.

2. RAPID METHOD FOR DETERMINING CHROMIUM IN STEEL

Principle.—The sample is dissolved in nitric acid containing about 2.5 mgs. of manganese as sulfate. The nitric acid solution is treated with sodium bismuthate under conditions such that the formation of permanganic acid indicates a satisfactory oxidation of the chromium, sulfuric acid is added, and enough hydrochloric acid to reduce the permanganic acid without affecting the chromic acid. The cold solution is then titrated with the electrometric apparatus as in Method 1.

Solutions Required.—*Nitric Acid* (d. 1.13) (*cf.* p. 50) containing 0.2 g. of manganese sulfate per liter.

Sulfuric Acid (d. 1.58) made by adding concentrated acid to 2.5 times as much water.

The other reagents are the same as in Method 1.

Procedure.—Dissolve 1 g. of the sample by heating with 50 c.c. of the nitric acid solution and boil 1 min. after solution is complete. Add 20 c.c. water and heat just to boiling. Remove from the hot part of the plate and add 2 g. sodium bismuthate. Boil gently at least 2 min. If the color of permanganic acid is not pronounced at the end of this time, make a second addition of sodium bismuthate and boil again.

The color of permanganic acid should be marked at the time of taking the next step in the determination. This consists in adding enough boiling water to make 200 c.c., 40 c.c. of dilute sulfuric acid and 15 c.c. of dilute hydrochloric acid. Boil 2 min. after the color of permanganic acid disappears. Then add finely crushed ice and titrate electrometrically.

NOTES AND PRECAUTIONS.—The method is applicable to steels containing 2.5 per cent of chromium and which have not been forged or subjected to complete heat treatment. In the latter case carbides cause low results. Heating a cast piece above the critical temperature, quenching and drawing do not prevent analysis by this method.

If vanadium is present this will be oxidized and titrated with chromium.

Manganese is added to the nitric acid to insure the presence of 0.3 to 0.6 per cent of manganese in the sample to be analyzed. The manganese, through the formation of permanganic acid, is a convenient indicator of the success of the oxidation. If present in amounts greater than 0.75 per cent, MnO_2 is precipitated in a form which resists solution by dilute hydrochloric acid. It is possible that the permanganic acid assists in the decomposition of carbides.

The 20 c.c. of water is added to facilitate the oxidation of the manganese to permanganic acid. If the water is added in a more dilute nitric acid, the dissolving of the sample is delayed and carbides are not attacked. If the amount of water is greater, the bismuthate and permanganic acid do not decompose the chromium carbides. If the amount of water is less, more manganese dioxide is formed and there is an incomplete oxidation of the chromium present as carbide.

When the amount of chromium carbide is small, one addition of sodium bismuthate will be sufficient. An index of the

presence of sufficient bismuthate is the persistence of the color of permanganic acid during 2 min. of gentle boiling. When it does not persist, a second addition must be made. Gentle boiling prevents a too great change in concentration by evaporation. In the case of samples taken from preliminary tests a second addition will generally not be necessary, but no rule as to this can be laid down.

When oxidation is complete and water is added, a precipitate of bismuth subnitrate appears. This dissolves upon the addition of sulfuric acid. At this point the color of the solution should indicate an appreciable quantity of undecomposed permanganic acid. Turbidity may be due to carbides or manganese dioxide. Carbides will not be present when the method is properly applied to the classes of steel for which it has been found suitable. Manganese dioxide will be formed only in small amounts under the conditions described, when the total amount of Mn present does not exceed 0.75 per cent. Such amounts as do form may be readily decomposed along with the permanganic acid by boiling two minutes after the addition of hydrochloric acid.

The sulfuric acid prevents the precipitation of bismuth oxychloride during boiling to decompose manganese compounds.

The finished solution should have a bright yellow or orange color, and turbidity or undissolved material should be due only to the presence of a precipitate of bismuth oxychloride.

3. DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD[1]

Principle.—Manganous nitrate formed by dissolving the steel in nitric acid, is oxidized by sodium bismuthate in the usual way and the permanganic acid is titrated with standard mercurous nitrate solution. With this reducing agent the permanganic acid appears to be reduced according to the following equation:

$$4\,MnO_4^- + 7Hg_2^{++} + 20H^+ \rightarrow 3MnO_2 + Mn^{++} + 14Hg^{++} + 10H_2O$$

$$\text{or } 4MnO_4^- + 7Hg_2^{++} + 32H^+ \rightarrow 3Mn^{++++} + Mn^{++} + 14Hg^{++} + 16H_2O$$

[1] KELLY and Others, *J. I. E. C.*, **10**, 19 (1918).

The manganese dioxide is not precipitated at the prescribed acidity and at a low temperature; it exists either in colloidal solution or as a sulfate of quadrivalent manganese.

Solutions Required.—The nitric acid and potassium permanganate solutions are the same as described in Chapter III, Method 1, but it is convenient to adjust the permanganate so that 1 c.c. = 0.0005 g. of manganese. The sulfuric acid is as in Method 2 above. The mercurous nitrate is prepared by dissolving 10.5 g. of mercurous nitrate in 150 c.c. of water and 2 c.c. of nitric acid; any undissolved salt is removed by decantation and the solution made up to 1 liter. Standardize the solution against standard potassium permanganate solution in the electrometric apparatus, or by precipitating with dilute sodium chloride in the presence of a little sodium acetate and filtering off the mercurous chloride precipitate into a weighed Gooch crucible. This precipitate may be dried at 150°.

Procedure.—Dissolve the steel in nitric acid and proceed exactly as described on page 52 until the excess of sodium bismuthate has been removed by filtration. Add a little ice and 50 c.c. of sulfuric acid (d. 1.58). At a volume of 250 c.c. and at a temperature below 40°, titrate in the electrometric apparatus with mercurous nitrate solution, as follows

Adjust the resistance to bring the beam of light from the potentiometer on the ground glass scale and then add the standard mercurous nitrate solution. The beam remains stationary, or shows a slight anomalous rise, until the end-point is approached. Thereupon the addition of mercurous nitrate causes the beam to move in the opposite direction from which it returns more or less slowly as the solution is stirred, until finally it remains off the scale altogether. The addition of a few drops of standard potassium permanganate solution causes it to return and the titration is finished by adding mercurous nitrate solution, drop by drop. The end-point is sharp, is not affected by chromates or vanadates but is influenced by rise of temperature, considerably more mercurous nitrate being required if the titration takes place at 80° than at 40°.

Computation.—If s represents the weight of sample taken, a the volume of mercurous nitrate solution used, of which 1 c.c. = f c.c. of standard permanganate, and b represents the volume of

permanganate solution used, of which 1 c.c. = p gm. of manganese, then

$$\frac{(a \times f - b)\, p \times 100}{s} = \text{per cent Mn}$$

Or, if the mercurous solution was standardized gravimetrically and 1 c.c. has been found to yield q. g. of Hg_2Cl_2 and the permanganate used is N-normal, then when a c.c. of mercurous nitrate and b c.c. of permanganate were used with s g. of steel,

$$\frac{4\ \text{Mn} \times a \times q - b \times \text{N} \times 0.011}{7\text{Hg}_2\text{Cl}_2 \times s} \times 100 = \text{per cent Mn}$$

or

$$\frac{.0665a - 1.1bN}{s} = \text{per cent Mn}$$

4. DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD[1]

This method is precisely the same in principle as the foregoing except that the manganese is converted to permanganate by means of ammonium persulfate in the presence of silver ions (*cf.* Method 1, p. 280) and is not reduced by adding hydrochloric acid. This method requires no filtration, as the excess of persulfate is decomposed partly by boiling and the excess causes a constant error. Moreover, although chromium is oxidized to chromate it does not interfere when mercurous nitrate is used and the end-point is determined electrometrically.

Procedure.—Dissolve 0.5 g. of steel (or 1 g. if the manganese content is below 0.5 per cent) in 65 c.c. of 6-normal sulfuric acid and oxidize the iron to the ferric condition by adding concentrated nitric acid, drop by drop, to the hot solution. After boiling 2 min., dilute to 200 c.c. with hot water, heat to boiling and add 10 c.c. of silver nitrate solution and 20 c.c. of ammonium persulfate as in Method 1. Boil 1 min., cool, add a little more sulfuric acid (about 60 c.c.) and titrate at 20° with mercurous nitrate solution as in Method 3.

Computation.—It is convenient to adjust the concentrations of the mercurous nitrate and potassium permanganate so that 1 c.c. of either is equivalent to 0.0005 g. of manganese. In the case of the permanganate, 39.33 c.c. will then be equivalent to 0.1200 g. of sodium oxalate. In this method the persulfate is not

[1] KELLY and Others, *loc. cit.*

decomposed completely for fear that some of the permanganate will be reduced as well. This persulfate causes a slight difference in the ratio between the permanganate and mercurous standard solutions but the effect does not vary appreciably with the small quantities of persulfate that are likely to be present. The ratio between the permanganate and mercurous nitrate solutions, therefore, should be established electrometrically and a little persulfate should be present. The computation requires no explanation if the solutions are equivalent and both equal to 0.0005 g. of manganese. A person without previous chemical training can learn to make one of these analyses after a few minutes of instruction.

5. DETERMINATION OF VANADIUM[1]

Principle.—By means of nitric acid of suitable concentration it is possible to oxidize 99 per cent of the vanadium to vanadic acid without oxidizing any chromium that may be present. The method is not quite as accurate as the other electrometric methods which have been described and empirical factors have to be assumed to allow for incompleteness of the oxidation and for the absorption of vanadium by tungstic acid, but the results are seldom more than 0.02 per cent in error when 2 per cent of vanadium is present. By means of standard ferrous ammonium sulfate solution, the vanadic acid is reduced to quadrivalent vanadyl salt and after adding a slight excess the endpoint is obtained by back titrations with a little potassium dichromate solution and a few drops of ferrous sulfate solution.

$$V + H_2SO_4 + H_2O \rightarrow VOSO_4 + 2H_2$$
$$3VOSO_4 + HNO_3 + 4H_2O \rightarrow 3HVO_3 + 3H_2SO_4 + 2NO$$
$$2HVO_3 + 2FeSO_4 + 3H_2SO_4 \rightarrow 2VOSO_4 + Fe_2(SO_4)_3 + 4H_2O$$

Solutions required.—*Potassium Dichromate.*—Dissolve 0.9609 g. of recrystallized potassium dichromate in distilled water and dilute the solution to exactly 1 liter in a calibrated flask. One cubic centimeter of this solution corresponds to 0.0010 g. of vanadium.

Ferrous Ammonium Sulfate.—Dissolve 8 g. of the salt and 50 c.c. of concentrated sulfuric acid in enough water to make 1 liter.

[1] KELLY and Others, *J. I. E. C.*, **11**, 632 (1919).

Adjust this solution daily so that it is equal in strength to the dichromate solution. The strength of the dichromate solution should be verified weekly.

Procedure.—If less than 0.5 per cent of vanadium is present, dissolve 2 g. of the steel in 100 c.c. of 6-normal sulfuric acid; with higher percentages of vanadium use half as large a sample and 80 c.c. of sulfuric acid. When the steel is all dissolved, oxidize the iron to the ferric state by adding 2 c.c. of concentrated nitric acid to the hot solution. Boil until the oxides of nitrogen are removed and until the tungstic acid is yellow, if any is present. Dilute with hot water to about 100 c.c. and add 40 c.c. of concentrated nitric acid. Boil this solution for an hour at such a rate that the volume does not fall below 100 c.c. Cool, dilute to 300 c.c. with ice water and titrate electrometrically.

Assume that the boiling with nitric acid oxidizes 99 per cent of the total vanadium content and that each per cent of tungsten present in the steel will absorb 0.001 per cent of vanadium. If difficulty is experienced in getting the end-point, 25 c.c. of 12-normal sulfuric acid may be added at the time of titration. It does no harm to boil the solution more than an hour but if the volume falls below 100 c.c. there is danger of some chromium being oxidized. In getting the end-point a slight excess of ferrous sulfate should be added in the first place, then a smaller excess of dichromate, finishing with ferrous sulfate solution added drop by drop. The first large movement is taken as the end-point.

6. THE DETERMINATION OF VANADIUM AND CHROMIUM IN FERRO VANADIUM[1]

In this method of analysis, the alloy is dissolved in nitric acid, a little hydrochloric acid is added to help remove carbide and hydrofluoric acid is used to dissolve silica. After the removal of these acids by evaporating with sulfuric acid, the solution is diluted to a definite volume and aliquot parts taken for further analysis. In one portion the chromium and vanadium are determined together as in Method 1 and in another portion the vanadium alone is determined as in Method 5. The computation

[1]Method of G. L. Kelley. Taken from the catalogue of F. H. Thomas Co., prior to its publications elsewhere (September, 1920).

will be explained on the assumption that standard solutions are used, each of which is equivalent to 1 mg. of chromium per cubic centimeter.

Procedure.—Dissolve 3 g. of the sample in 75 c.c. of nitric acid (d. 1.13). When solution is almost complete, add 10 c.c. of HCl to assist in decomposing carbides. After the volume has been reduced about one-half, add a few drops of hydrofluoric acid to remove silica. Then add 50 c.c. of sulfuric acid and evaporate until fumes of sulfuric acid appear, with the object of removing all hydrochloric acid. Dilute in a standardized flask with water to 1 liter. With a standardized pipette remove two 100-c.c. portions.

To 100 c.c., add 20 c.c. sulfuric acid and water to make 300 c.c. Boil and add silver nitrate and ammonium persulfate to oxidize chromium, vanadium, and manganese. After 10 min. boiling, add 3 c.c. of 3-normal hydrochloric acid to decompose permanganic acid. Boil 10 min. longer, cool, add 25 c.c. of sulfuric acid, and titrate at 5°C. with a ferrous sulfate solution equivalent to dichromate solution containing 0.001 g. Cr per cubic centimeter. The titration includes chromium and vanadium. Divide the titration by 3 and multiply by 2.943. This converts both chromium and vanadium into the equivalent percentage of vanadium.

To a second 100-c.c. portion add a few cubic centimeters of ferrous sulfate solution to reduce any chromium existing in the oxidized condition and follow this with 20 c.c. of sulfuric acid and 40 c.c. of nitric acid together with water enough to give a volume of 200 c.c. Evaporate by boiling quietly at such a rate that in one hour the volume is reduced to 100 c.c. Under these conditions 99.5 per cent of the vanadium is oxidized. Cool to 5°C. and titrate with ferrous sulfate. To calculate, divide by 0.995 and by 3 and multiply by 2.943. This gives the percentage of vanadium.

The percentage of chromium may be calculated by subtracting the per cent obtained by the second oxidation from that obtained by the first and dividing the difference by 2.943.

NOTES AND PRECAUTIONS.—In oxidizing with ammonium persulfate and silver nitrate it is important to have the sulfuric acid and water in the proportions given. After adding the ammonium persulfate, and after adding the hydrochloric acid, the solution should be boiled at least 10 min.

The concentration of nitric acid, the initial and final volumes, and the rate of evaporation are important steps in securing a regular oxidation of vanadium by nitric acid.

Any insoluble matter in the ferro-vanadium suspected of containing vanadium should be fused with sodium peroxide. After leaching boil the alkaline solution for 20 min. Then acidify with sulfuric acid and add to the main portion of the solution before making up to volume. It is rare that this treatment is necessary.

If a solution, containing 2.883 g. of potassium dichromate in 1 liter should be used, each cubic centimeter would correspond to 1 per cent of vanadium when a sample weighing 3 g. is used.

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The Electrometric Determination of Carbon in Steel[1]

This method is based upon the measurement of the change in electrical resistance in a solution of barium hydroxide from which a part of the barium has been precipitated as carbonate by carbon

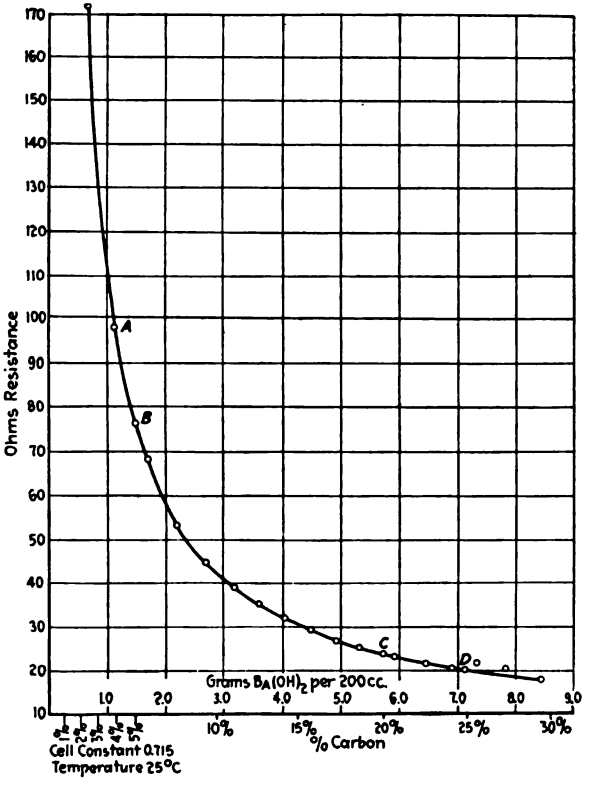


Fig. 42.

dioxide formed by direct combustion of steel in an electric furnace. It is an electrometric method because the final estimation is based upon two measurements of electrical resistance but it is different from the preceeding methods which all depended upon

[1] Cain and Maxwell: *J. I. E. C.*, **11**, 852 (1919); *Technologic Paper* No. 141, U. S. Bureau of Standards.

the measurement of electrode potential. The fundamental chemical reaction involved is

$$Ba^{++} + 2OH^- + CO_2 \rightarrow BaCO_3 + H_2O$$

Barium hydroxide in aqueous solution exists chiefly as barium and hydroxyl ions but barium carbonate is insoluble; the conductance of the solution, which is the reciprocal of the resistance value, falls as these ions are removed. The temperature of the solution also has a marked effect upon the conductance, changing about 1.7 per cent for 1° of temperature change. Figure 42 shows the

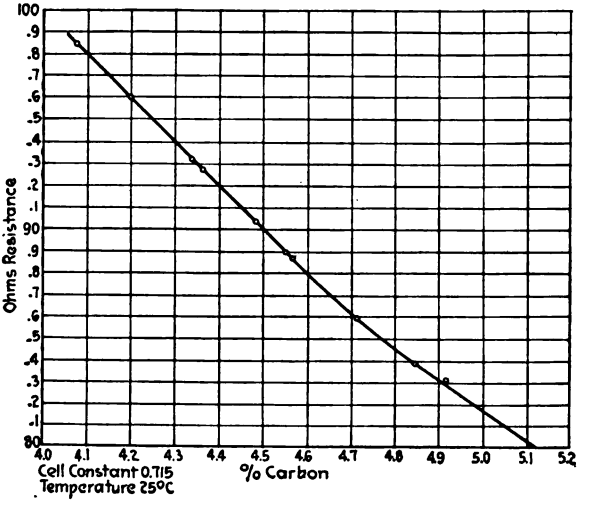


FIG. 43.

relation between the electrical resistance and barium hydroxide concentration.[1] The curve shows that these changes in resistance

[1] The bottom values for the abscissas in Fig. 42 are expressed in what Cain and Maxwell have called the "equivalent per cent carbon." This term was chosen for convenience in using a nomograph scale. It is based on the assumption that exactly 200 c.c. of barium hydroxide solution are present in the absorption tube, which is also used for the resistance measurement, and that a sample of steel weighing exactly 2 g. is taken for analysis. If p represents the weight of $Ba(OH)_2$ in grams present in the solution, then $\frac{C \times p \times 100}{Ba(OH)_2 \times 2}$ is the "equivalent per cent carbon."

are about six times as marked for corresponding changes in concentration on the portion of the curve lying between *A-B* as on the portion *C-D*. Solutions to the left of *A* contain so little barium hydroxide that they are not sufficiently effective as absorbents for carbon dioxide.

The portion of the curve selected for use by this method is again shown in Fig. 43 and the data from which this curve was drawn is given in Table 1.

TABLE I.—DATA FOR RESISTANCE-CONCENTRATION CURVE OF $Ba(OH)_2$ SOLUTIONS IN THE REGION 4 PER CENT TO 5 PER CENT CARBON EQUIVALENT STRENGTH

CELL CONSTANT = 0.715

$Ba(OH)_2$ per 200 c.c. solution, grams	Equivalent per cent carbon	Temperature degrees, Centigrade	Observed resistance, ohms	Corrected resistance, ohms
1.164	4.075	23.6	100.9	98.49
1.198	4.194	24.2	97.4	96.08
1.239	4.337	24.2	94.6	93.26
1.242	4.348	23.2	95.8	92.81
1.280	4.482	24.4	91.4	90.42
1.286	4.500	26.6	87.6	90.01
1.301	4.553	27.5	85.3	88.92
1.303	4.559	26.4	86.8	88.79
1.346	4.712	25.1	86.0	86.06
1.385	4.848	25.8	82.7	83.90
1.403	4.912	24.4	84.2	83.94
1.460	5.110	23.1	82.8	80.11

The resistance of barium hydroxide solutions decreases with rise in temperature. Cain and Maxwell have determined the resistances of barium hydroxide solutions at 20°, 25° and 30° at concentrations corresponding to approximately 4.0, 4.25, 4.50, 4.75 and 5.0 equivalent per cent carbon[1] and the data obtained is

[1] When the concentration of the barium hydroxide is expressed in this way, the percentage of carbon present in a 2-g. sample of steel is found by subtracting the "equivalent carbon concentration" of the cell after the combustion from the "equivalent carbon concentration" at the start. If a 2-g. sample of steel contained 5 per cent carbon it would precipitate all the $Ba(OH)_2$ in 200 c.c. of barium hydroxide solution containing 5.0 equivalent per cent carbon.

given in Table II. The values for α and β given in the table were obtained by substituting the experimental temperatures, t, and resistances, R, in the equation

$$\frac{1}{RT} = \frac{1 + \alpha\,[t - 25] + \beta\,[t - 25]^2}{R_{25°}}$$

TABLE II.—DATA FOR TEMPERATURE COEFFICIENTS OF RESISTANCE

Concentration of $Ba(OH)_2$ solution per cent Centigrade approximate	Temperature degrees Centigrade	Resistance ohms	α	$\beta \times 10^{-4}$
5.00	20	135.25		
	25	124.02	0.01674	0.2687
	30	114.37		
4.75	20	142.18		
	25	130.36	0.01680	0.3505
	30	120.16		
4.50	20	149.07		
	25	136.62	0.01686	0.3085
	30	125.91		
4.25	20	156.18		
	25	143.07	0.01687	0.1652
	30	131.89		
4.00	20	165.18		
	25	151.28	0.01687	0.0898
	30	139.48		

If the temperature of the solution lies between 15° and 25° the β term in the correction formula can be neglected but this value becomes appreciable if the solution is at a temperature is more than 10° away from 25° which is chosen as a suitable standard temperature in this method of analysis. If the laboratory temperature is above 35° the stock bottle 14 in Fig. 45 should be placed in cold water. The correction formula for changing the observed resistance value, R, to that which would prevail at 25°, R_{25}, can then be found by the formula

$$R_{25} = Rt[1 + \alpha(t - 25)] \text{ in which } \alpha = 0.0168$$

The simplest way of determining the percentage of carbon equivalent to any resistance measurement is by means of the

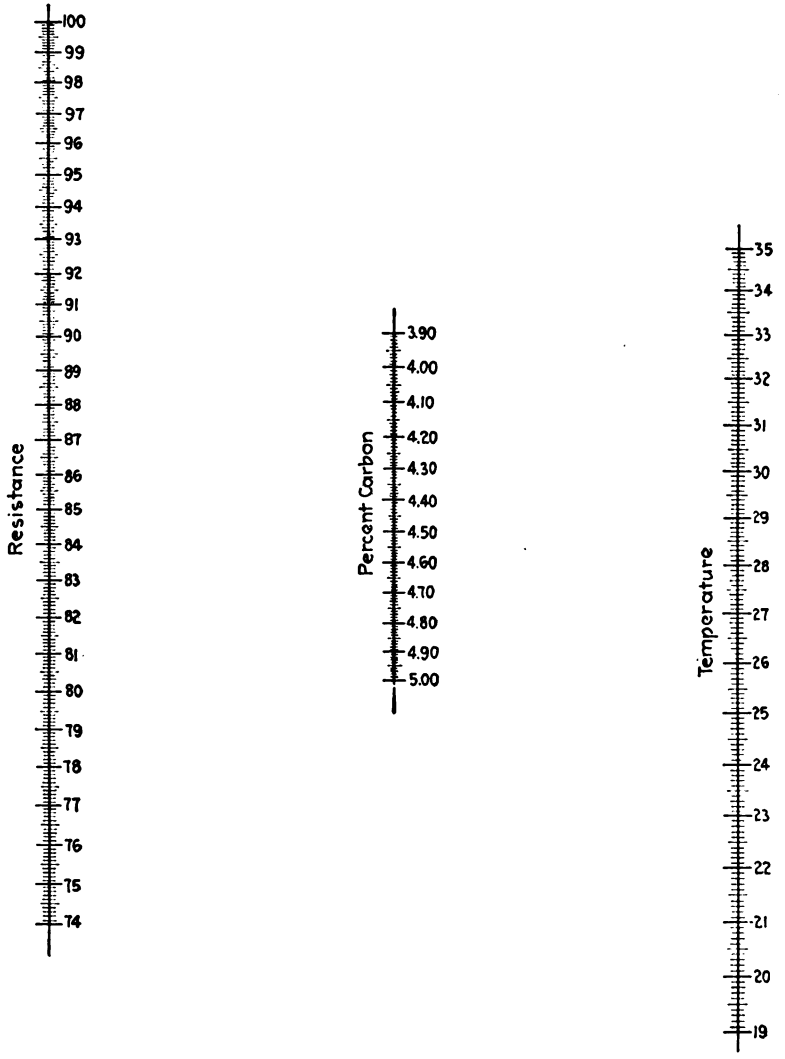


FIG. 44.—Nomograph chart.

nomograph shown in Fig. 44, p. It is not necessary, here, to go into the mathematical discussion of the method by which

this scale is constructed but the use of the nomograph is very simple. A straight edge is made to connect the observed values for temperature and resistance and the intersection with the third (middle) ordinate gives the concentration of the solution in terms of carbon percentage; this may be termed the first concentration. After the combustion is ended a similar set of readings is taken and subtraction of the second concentration reading from the first gives directly the per cent of carbon if a 2-g. sample has been taken; or, if a 1-g. sample has been used, the result is multiplied by two. The scales can be read to 0.005 per cent C, 0.05°C., and 0.05 ohm. It was found by comparison of chart readings in a number of cases with the resistances computed by the above formula that the error of the chart is less than 0.005 per cent carbon.

The entire apparatus as designed by Cain and Maxwell[1] is shown in Fig. 45.

The outfit consists of the Hoskins type low-voltage furnace (1), fed by alternating current from the transformer (2), controlled by the rheostat (3) in the primary circuit. A fused silica combustion tube (4) in this furnace has inserted in its forward end a roll of 80-mesh copper oxide gauze about 4 in. long, placed so it is heated by conduction from the hot zone of the furnace to from 300 to 400°C. This removes sulphur compounds and also ensures complete combustion of any carbon monoxide that may be formed. Oxygen from the cylinder (5) passes successively through the reducing valve (6), the soda-lime tower (7) and the bubble counting device (8), into the furnace. The combustion is made in nickel, clay, alundum, platinum, or other suitable boats filled with 90-mesh RR Alundum, Blue Label, sand. A nickel or alundum sleeve, fitted inside the tube in the region occupied by the boat, protects the tube from spattered oxides, or, in most cases, spattering of oxides in the tube can be prevented by covering the steel, after placing it on the alundum sand, with some more of the alundum sand. Some method of protection of the tube, such as recommended, must be provided in order that the rapid combustion produced by the procedure described later does not ruin the tube by the throwing off of fused oxides.

[1] *Loc. cit.* The illustration and description of the apparatus were furnished by the A. H. Thomas Co. of Philadelphia for use in this book.

The oxygen next passes into the absorption vessels through stopcocks (9). The absorption vessels (10) and 10′) are provided with electrodes (11) and (11′) and thermometers (12) and (12′), and are connected by cocks (13) and (13′) with the reservoir (14) containing stock barium hydroxide solution, and with bottle (15) which receives used or spent solution. Filling and emptying of

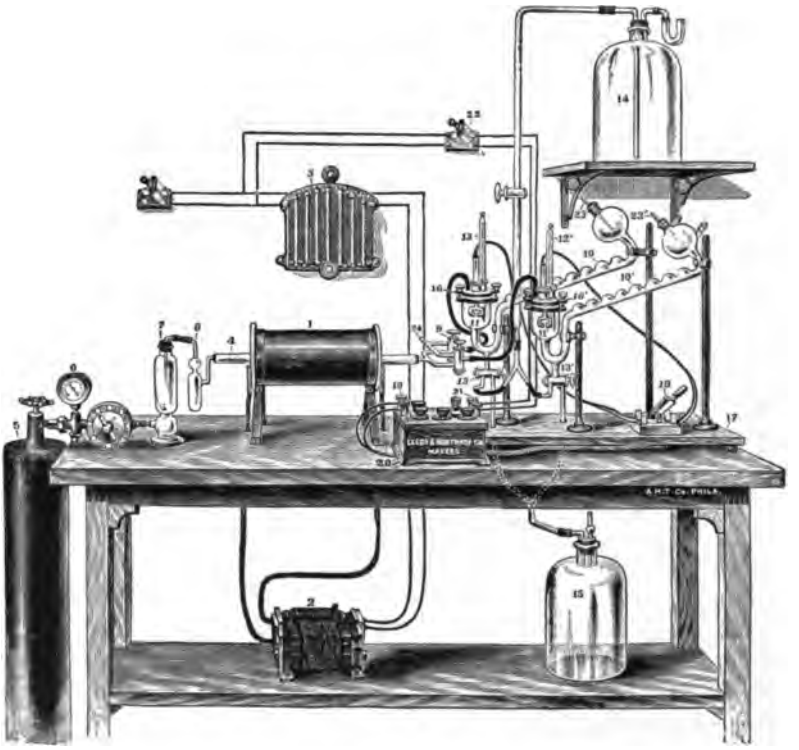


FIG. 45.

absorption tubes must in all cases be done through stopcocks (13) and (13′). In no case must the covers (16) and (16′) be removed for filling and emptying, nor must the absorption vessels be removed from the support (17). This is very important. The electrodes of the absorption vessels are connected through the double-throw switch (18) with the binding posts (19) of the special resistance measuring bridge (20). The other two binding

posts (21) of this bridge are connected through the switch (22) with a 110-volt alternating current line (25 or 60-cycle). The bulbs (10) and (10′) of the absorption vessels are fitted with single perforated rubber stoppers, carrying tube (23) and (23′). A rubber tube connected to a soda-lime tower, which in turn is connected to the laboratory air supply, can be slipped alternately on to either of these glass tubes or the arm (24) of stopcock (9).

Procedure.—The two absorption vessels are filled to the 200-c.c. mark with barium hydroxide solution from the stock bottle 14, Fig. 45. Oxygen or air freed from carbon dioxide is passed for a few seconds to mix the solutions, and their temperatures and resistances are then recorded. In the meantime the combustion boat filled with alundum sand has been preheating in the furnace, which for this work should be maintained continuously at 1,050 to 1,100°C., preferably the latter temperature.[1] This is an extremely important point, for if the temperature is too low or the oxygen is not pure or is not admitted at 300 to 400 c.c. per minute after the combustion starts, the rapid combustion essential to successful absorption, can not be secured. The boat is removed from the furnace, and when at a low-red heat the sample is distributed on the alundum[2] and the boat replaced in the furnace and left to preheat, without oxygen passing, while the next sample is being weighed. Oxygen is now passed at the rate of 300 to 400 c.c. per minute for the next 2 min.; then stopcock 13, Fig. 45, is turned to position 2, which admits carbon-dioxide-free air; this should pass at the same rate as the oxygen. During this combustion period, if directions have been followed, all carbon dioxide will have been removed from the furnace, but some still remains in the large bulb of the absorption apparatus; the air removes this. The advantage of the use of air at this stage is obvious: a saving of oxygen is effected and the furnace is immediately available for burning the next sample. While air

[1] The melting point of gold is a convenient temperature check. If this metal is not melted the temperature is too low. See cited paper by Cain and Maxwell.

[2] Experience has shown that no loss of carbon occurs unless the sample contains dust; with most steels this can first be removed without causing an error in the carbon determination. This point should always be tested, however, in burning new steels.

is passing through the first tube (1½ to 2 min. is necessary for this) the combustion of the next sample proceeds as already directed, using the second absorption tube. The second reading of resistance and temperature on the first tube then follows, and if the solution is not too dilute it can be used for absorbing the carbon dioxide from other samples; otherwise, a little is allowed to flow into the reservoir *G*, and the tube filled to the mark again with fresh solution. Of course it is an economy in time for the operator, wherever possible, to choose conditions (weight of sample, carbon content of same, etc.) so as to get the maximum number of determinations for a single filling, since in this way the second resistance and temperature readings serve as initial values for the next combustion, and so on. The solution should not be used when it is more dilute than corresponds to 4 per cent carbon (*i.e.*, 99.5 ohms at 25°; see nomograph, Fig. 44, for the limiting resistances corresponding to other temperatures), since its absorptive power at rapid rates of passage of the oxygen is then less, and some carbon dioxide may be lost. The data relating to combustions should be recorded as obtained. It is convenient to use a tabular form or record showing (1) designation of sample, (2) weight taken, (3) cell used, (4) initial temperature, (5) final temperature, (6) initial resistance, (7) final resistance, (8) initial concentration, (9) final concentration, (10) carbon percentage in sample, and (11) remarks. There is ample time for entering this information while other operations are going on. A very good way is to enter "final temperature" below "initial temperature," and "final resistance" after "initial resistance" for each sample, since this relates these quantities in an easy manner for reading the nomograph.

The speed of the method naturally depends on the skill of the operator and the ingenuity displayed in arranging a cycle of operations which secures the best speed under his working conditions. Operators when working on a series of Bureau of Standards analyzed samples averaged one determination per 4½ to 5 min. The accuracy of results is shown in Table III.

TABLE III.—RESULTS BY ELECTROLYTIC RESISTANCE METHOD

Sample used	Grams used	Bureau of Standards value for carbon (average by direct combustion), per cent	Value by electrolytic resistance method	Analyst
11a	2.0	0.223	0.21	Maxwell.
11a	2.0		0.21	
12b	2.0	0.409	0.41	Swindells.
	2.0		0.41	
	1.0		0.42	
14a	2.0	0.813	0.81	Swindells.
	1.0		0.82	
	2.0		0.80	Maxwell.
16a	0.5	0.990	1.00	Cain.
	0.5		1.00	
	1.0		1.00	
	2.0		0.98	
21a	2.0	0.617	0.62	Cain.
21a	2.0		0.62	Maxwell.
Sugar (grams carbon).	0.00421		0.0046	Maxwell.
	0.00421		0.0042	
	0.00421		0.0040	

OPERATING SUGGESTIONS

1. Stock barium hydroxide solutions are conveniently made in one to two carboy lots by adding solid barium hydroxide to the carboy nearly filled with water (agitating with air) until the equivalent strength approaches 5 per cent carbon. Subsequent additions can then be made by adding a saturated barium hydroxide solution. Of course, it is not necessary to make up exactly to the equivalent of 5 per cent carbon. An approximation to this is all that is desired. The strength of the solution is determined from time to time during the standardization by running a portion of the solution into the cell and measuring its resistance. If a setup like that shown in Fig. 45 is used in measuring the resistance, it is not necessary to remove bottle 14 from the shelf or to break any of the connections during these operations. If it is desired to economize in the use of barium salt, the waste solution in bottle 15 can be brought up to strength

as described, after first decanting it off from the barium carbonate that has settled out. A still further economy can be effected by drying and calcining to oxide the precipitated barium carbonate. This oxide can then be used again.

2. The cell constants should be checked from time to time. This may be done (1) by burning standard samples or (2) by determining the resistance of a N/10 solution of pure potassium chloride. This solution should be prepared on the day it is to be used, since stock solutions have been found to change during the course of this work. Table IV shows the resistivities at

TABLE IV.—SPECIFIC RESISTIVITY OF N/10 KCl SOLUTION AT VARIOUS TEMPERATURES

(From Landolt-Börnstein Physik. Chemische Tabellen 4 Ed., p. 1117.)

Temperature	Resistance, ohms	Temperature	Resistance, ohms	Temperature	Resistance, ohms
15.0	95.42	22.0	82.30	29.0	72.10
16.0	93.28	23.0	80.71	30.0	70.82
17.0	91.32	24.0	79.11	31.0	69.59
18.0	89.37	25.0	77.64	32.0	68.40
19.0	87.49	26.0	76.16	33.0	67.20
20.0	85.69	27.0	74.79	34.0	66.09
21.0	83.96	28.0	73.42	35.0	64.98

various temperatures of N/10 potassium-chloride solutions. The cell constant is computed from the formula: $R = NS$, or $N = \frac{R}{S}$ where R is the observed resistance, N the cell constant, and S the resistivity, taken from Table IV, for the same temperature. If a change in cell constant has taken place, it is most probable that the electrodes need replatinizing. Directions for this are given in paragraph 4 of this section. If Method 1 is used, any marked deviation from the correct carbon value of the standard steel may be due to a change in the cell constant, and this should then be checked by Method 2, unless it is suspected that the error in the carbon determination is due to some other cause. No deviation of cell constants has been observed until after several months' use, and then the change is sudden and erratic. When

the cell constant changes, it should be brought back to the original value.

The adjustment of the cell constant is made by moving the electrodes up and down after loosening the stuffing box; a marked change takes place as they approach the meniscus.

3. If the absorption vessels are not to be used for some time, they should be cleaned with hydrochloric acid (not over 2 to 3 per cent HCl) followed by distilled water. Extreme care should be taken that none of the hydrochloric acid or chlorides enter the reservoir for waste barium hydroxide solution if this is to be used again.

4. To platinize the electrodes, the cap carrying them is removed from the cell, and they are first cleaned with sulphuric and chromic-acid mixture, followed by distilled water. Then they are immersed in a vertical position in a solution made of 100 g. water, 3 g. chloroplatinic acid, and 0.02 to 0.03 g. lead acetate. Current is passed through the solution by connecting the electrodes to three dry batteries in series. The current is passed for 5 min., reversing every half minute. Finally, an auxiliary platinum electrode is introduced and current passed with this as anode for another 2 min., after which the electrodes are washed thoroughly with distilled water and are then ready for use.

CHAPTER XXII

NON-FERROUS ALLOYS

The preceding chapters have dealt with the analysis of ferrous alloys and the methods described were applicable to the estimation of small quantities of various elements in the presence of a large quantity of iron. In the analysis of commercial copper alloys, the quantity of iron present has little if any effect upon the determination of the other constituents. Moreover, in the analysis of copper alloys special emphasis is placed upon the quantitative determination of the most important constituents, whereas in the analysis of iron and steel the quantity of iron present is rarely determined by direct analysis.

Brass is an alloy of copper and zinc and many samples of brass contain less than one-tenth of 1 per cent of other constituents. The copper and zinc used to make the alloy, however, are never absolutely pure and brass usually contains traces of lead, tin, cadmium, arsenic, iron, etc. Bronze is usually defined as an alloy of copper and tin but other elements are often added intentionally and certain alloys which look like bronze have been classified as such although they may contain no tin. Thus aluminium bronze is copper alloyed with 5 to 10 per cent of aluminium. Phosphor-bronze, on the other hand, is a copper-tin alloy to which a little phosphorus has been added intentionally and manganese bronze is a copper-tin alloy to which manganese has been added.

Inasmuch as small quantities of antimony are likely to be present in commercial brasses and bronzes it has seemed advisable to extend this chapter somewhat and include the analysis of a typical tin-antimony alloy in which the copper content is low.

Copper is so far below hydrogen in the electrochemical series of the elements that it does not dissolve in dilute hydrochloric or sulfuric acid[1] unless some other substance is present containing

[1] Copper reacts with hot, concentrated sulfuric acid to form cupric sulfate and sulfur dioxide. In this case, the sulfate ion acts as oxidizing agent.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2 \uparrow$$

an ion which has greater oxidizing power than the hydrogen ion.

The most appropriate solvent for copper and its alloys is nitric acid. The copper is oxidized to the cupric condition and the nitrate ion is reduced. If an excess of concentrated nitric acid is used, nitrogen peroxide is the principal reduction product, but with dilute nitric acid, nitric oxide is formed:

$$Cu + 2NO_3^- + 8H^+ \rightarrow Cu^{++} + 2NO \uparrow + 4H_2O$$

The equation written in this form shows that eight molecules of nitric acid are required to react with 1 atom of copper but that only two molecules of nitric acid act as oxidizing agent.

The behavior of tin and antimony toward nitric acid is characteristic. Cold, dilute nitric acid dissolves tin slowly, forming stannous and ammonium nitrates:

$$3Sn + 20NO_3^- + 10H^+ \rightarrow 3Sn^{++} + NH_4^+ + 3H_2O$$

With hot, 6-normal nitric acid (d. 1.2) stannic nitrate is formed but this undergoes hydrolysis and "metastannic acid" is precipitated. The entire reaction may be expressed as follows:

$$15Sn + 20NO_3^- + 20H^+ + 5H_2O \rightarrow 3(H_2SnO_3)_5 + 20NO \uparrow$$

Stannic hydroxide is an insoluble, amphoteric substance with colloidal properties. When formed by the addition of caustic alkali to the solution of a stannic salt, it probably corresponds to the composition, $Sn(OH)_4$, and in this condition it dissolves readily in hydrochloric acid and in caustic alkali soltuion. By drying over sulfuric acid it becomes changed to α-metastannic acid, H_2SnO_3, and this compound in acid solution polymerizes into β-metastannic acid, $(H_2SnO_3)_5$. In the last-mentioned condition, stannic hydroxide is least soluble in acid and in alkali. The precipitate produced by boiling tin with moderately concentrated acid contains nitric acid and appears to correspond to the formula $Sn_5O_5(OH)_8(NO_3)_2$ but by washing with water the nitric acid can be removed[1] and the precipitate then corresponds to the formula, $(H_2SnO_3)_5$ which may be written:

$$Sn_5O_5(OH)_{10}$$

[1] *cf.* A. KLEINSCHMIDT, *Monatsh*, **39**, 149–78 (1918).

The behavior of antimony to nitric acid is similar. Antimonic hydroxide is amphoteric, insoluble and colloidal. The precipitate formed by treating antimony with nitric acid is antimony tetroxide, Sb_2O_4, and may be regarded as antimonous antimonate, $Sb{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}Sb{-}O{-}Sb{=}O$.

If an alloy dissolves completely in nitric acid, and no precipitate forms upon heating the solution, it is safe to assume that antimony and tin are absent. When tin or antimony is present, however, the precipitated metastannic acid or antimony tetroxide is rarely pure. These colloidal precipitates have the property of adsorbing dissolved substances to a marked degree. Thus phosphoric and arsenic acids are adsorbed and are to be found in the residue when antimony or tin is present. To a lesser degree other elements, such as titanium, iron and even copper, are likely to be adsorbed.

The colloidal properties of metastannic acid not only explain why it is rarely obtained pure as a result of dissolving an alloy in nitric acid but they also account for the fact that certain substances interfere with the formation of the gelatinous precipitate and tend to keep it in solution. Hydrochloric acid is one of the most efficient means of causing the "peptonization" or dissolving of the precipitate but small quantities of iron have also been found to prevent complete precipitation. It has been stated, for example, that the precipitation of metastannic acid is never complete if the original alloy contains as much as 0.25 per cent of iron.

The quantitative estimation of aluminium, antimony, arsenic, copper, iron, lead, manganese, nickel, phosphorus and zinc in typical "non-ferrous alloys" will be discussed in this chapter, the term "non-ferrous" being used merely to contrast the alloys with those in which iron is the basic constituent. In previous chapters the determination of each constituent has been discussed for the most part without regard to whether the same weighed portion of metal can be used for the determination of several constituents. In the analysis of non-ferrous alloys, it is the exception rather than the rule when one portion of the material is used for only one determination. In prescribing directions for

analysis, therefore, it is necessary not only to bear in mind the possibility of interference due to the presence of other constituents but also to consider whether these other constituents had best be removed previously or subsequently. Owing to this dependence of one determination upon another it has been difficult to decide upon a wholly logical order of treatment and it was finally decided to discuss the above ten elements in alphabetical sequence but this involves the analysis of metal containing elements to be discussed later, so that the order is not followed strictly.

ALUMINIUM

The metal aluminium is dissolved by dilute hydrochloric acid, forming aluminium chloride, but it is less soluble in dilute sulfuric acid and becomes passive when treated with nitric acid, probably because a closely adherent oxide film is formed by the action of nitric acid. Aluminium dissolves easily in caustic alkali solution forming sodium or potassium aluminate. Many schemes of analyzing commercial aluminium, or an alloy in which aluminium forms the major constituent, are based upon preliminary treatment with sodium hydroxide to dissolve the aluminium and zinc; this leaves most of the other constituents in the insoluble residue. The determination of aluminium in ferrous alloys has been discussed in Chap. XIV. It will lead us too far to consider the analysis of commercial aluminium ware or of alloys containing high percentages of aluminium. Here, merely a method for the analysis of aluminium bronze will be described.

ANALYSIS OF ALUMINIUM BRONZE

Procedure.—Dissolve 1 g. of the alloy in 10 c.c. of aqua regia. To the resulting solution add 5 c.c. of concentrated sulfuric acid and evaporate till heavy fumes are obtained. Cool, dilute to about 50 c.c., boil until the sulfates have all dissolved, filter and wash thoroughly with hot water. The residue on the filter paper is usually silica which can be ignited and weighed.

Remove the copper by electrolysis as described below under Copper.

To the filtrate add 2 or 3 g. of disodium phosphate and ammonium carbonate solution until a small permanent precipitate is

obtained. Dissolve this precipitate by adding a few drops of hydrochloric acid and add about 1 c.c. of 6-normal acid in excess. Dilute to 300 c.c., add 5 g. of sodium thiosulfate and heat to boiling. Add 20 c.c. of 6-normal acetic acid, boil 10 min., to coagulate the sulfur and filter. Wash the precipitate with hot water until the washings give no test for chloride. Ignite and weigh as $AlPO_4$ containing 22.19 per cent Al.

This method of precipitation has been explained in Chap. XIV.

ANTIMONY

The proper solvent for antimony and its alloys is aqua regia by which it is converted into chloride. Nitric acid, as already explained, converts antimony into Sb_2O_4 which dissolves slightly in concentrated acid but is practically insoluble in dilute nitric acid. The antimony present in alloys containing small quantities of this element may be determined in the residue obtained, as in the analysis of bronze, by treatment with nitric acid. The separation of antimony from copper and similar metals can also be effected by taking advantage of the fact that antimony sulfide, although insoluble in dilute acids, dissolves in alkali sulfide solution, or more readily in alkaline polysulfide, forming, in the latter case, alkali thioantimonate. The gravimetric separation of antimony and tin is usually based upon the fact that antimony sulfide is precipitated more readily than tin sulfide from acid solutions. Thus the classic method of F. W. Clarke is based upon the precipitation of antimony sulfide from a solution containing oxalic acid.

Antimony may be determined electrolytically, gravimetrically or volumetrically. The electrolytic method depends upon the deposition on the cathode from a sodium sulfide solution to which some such substance as potassium cyanide is added to react with polysulfides formed at the anode. The gravimetric determination is based upon the ignition of a pure antimony sulfide precipitate in a stream of carbon dioxide gas at about 230°; in this way dry Sb_2S_3 is obtained. The volumetric determination may be based upon (a) the oxidation of antimony from the trivalent condition to the quinquevalent condition, by treatment with potassium permanganate if the titration is done in acid solution or by iodine in neutral solution or (b) upon the reduction

of quinquevalent antimony by potassium iodide in acid solution and titration of the liberated iodine with sodium thiosulfate. It is interesting to note that when antimony pentasulfide dissolves in hydrochloric acid, antimony trichloride is formed which unites with hydrochloric acid to form soluble complexes. In an acid solution tin is much more readily oxidized than antimony. By dissolving a mixture of antimony and tin in hot sulfuric acid and shaking in the air, the tin is oxidized to the stannic condition and the antimony left as trivalent salt. Metallic antimony is often added to reduce tin from the stannic to stannous condition and in the resulting acid solution tin can be oxidized by iodine without affecting the antimony trichloride present. To illustrate the determination of antimony in alloys two methods for the examination of bearing metal, or an alloy of lead, tin, antimony and copper will be described.[1]

ANALYSIS OF BEARING METALS

As solvent for the alloy, prepare the following solution: Dissolve 20 g. of potassium chloride in 500 c.c. of water, mix with 40 c.c. of concentrated hydrochloric acid and add 100 c.c. of concentrated nitric acid. Dissolve 1 g. of the finely divided alloy in 70 to 100 c.c. of the solvent, heating to near the boiling point. Boil gently until the metal is all dissolved and the volume of the solution is reduced to 50 c.c. Add 5 c.c. of concentrated hydrochloric acid and cool by placing the beaker in cold water. When most of the lead has precipitated as lead chloride, preferably after standing over night, slowly add 50 c.c. of 95 per cent alcohol while constantly stirring. Continue stirring a few minutes and place the beaker in ice water for 10 min. Add 50 c.c. more of alcohol in the same way as before and allow to stand 20 min. in ice water. Filter through a 9-cm. filter into an 800-c.c. beaker. Wash three times by decantation with a mixture of concentrated hydrochloric acid and four times as much alcohol. The precipitate contains all but about 3 mg. of the total lead content. Ordinarily, this correction may be applied without attempting to recover the last traces of lead.

Preserve the filtrate for the determination of antimony, copper and tin.

[1] The methods are recommended by the American Society for Testing Materials.

Determination of Lead.—Wash the lead chloride back into the original beaker and thoroughly wash the filter paper with hot water and then twice with hot ammonium acetate solution (1 vol. conc. ammonium hydroxide + 1 vol. water + 80 per cent acetic acid until the solution is barely acid to litmus). A clear solution should be obtained; as little as 1 mg. of tin or antimony will cause turbidity. Add 15 c.c. of saturated potassium dichromate solution, heat until the precipitated lead chromate is of a good orange color, filter into a weighed Gooch crucible and wash with water and dilute alcohol. Dry at 110° and weigh. Calculate to lead by the empirical factor 0.6375.

Precipitation of Copper and Antimony.—Evaporate the filtrate from the lead chloride to dryness. Add 2 g. of solid potassium hydroxide dissolved in 10 c.c. of water and after a few minutes add 20 c.c. of 3 per cent hydrogen peroxide. Test the solution with litmus to make sure that it is alkaline and heat on the water bath for 20 min. Add 10 g. of ammonium oxalate, 10 g. of oxalic acid and 200 c.c. of water. Boil and introduce hydrogen sulfide into the hot solution for 45 min. This serves to precipitate the antimony and tin as sulfides leaving the tin in solution. The lead which was not precipitated as lead chloride is usually precipitated as sulfide at this stage, but if only a little copper or antimony is present, it may remain in solution with the tin. Filter and wash the sulfides of antimony and copper with hot water containing hydrogen sulfide.

Determination of Tin.—Concentrate the filtrate to about 100 c.c. and if more than 0.5 g. of tin is present, add 5 g. more of oxalic acid. Electrolyze over night with a gauze cathode and a current of about 0.5 ampere. If the solution is alkaline in the morning, the tin is probably all precipitated, but tin is not deposited well from an alkaline solution. Remove the electrode, wash with water and alcohol, dry at 100° and weigh as metallic tin. Add 5 g. of oxalic acid to the electrolyzed solution, heat to boiling and again electrolyze to see if any tin was left in the solution.

Determination of Copper.—Wash the precipitated antimony and copper sulfides back into the beaker in which the precipitation took place, using as little water as possible. Add 2 g. of potassium hydroxide dissolved in 10 c.c. of water. Heat until the insoluble residue of copper sulfide is distinctly black and then

filter through the same filter that was used to collect the precipitate of copper and antimony sulfides, catching the filtrate in a 300-c.c. Erlenmeyer flask. The copper is now on the filter as copper sulfide and the antimony is in the filtrate and as potassium thioantimonate. The copper sulfide precipitate usually contains a little lead sulfide. Ignite the precipitate and filter in a porcelain crucible and dissolve the oxides in 2 c.c. of 6-normal nitric acid. Dilute the solution to 50 c.c. and determine the copper (and lead) as described under Copper.

Determination of Antimony.—The solution of potassium thioantimonate obtained by the above treatment should not exceed 40 c.c. in volume. Add 50 c.c. of concentrated hydrochloric acid and boil for a few minutes to volatilize any arsenic as trichloride. The antimony chloride is left in the trivalent condition in the form of a complex such as $HSbCl_4$. The hydrogen sulfide from the decomposition of the thioantimonate serves to reduce traces of arsenic to the trivalent condition. Add 25 c.c. more of hydrochloric acid and 1 g. of potassium chlorate. Boil until the solution is colorless and the chlorine dioxide is all expelled. Filter through mineral wool into another 300-c.c. flask if sulfur has deposited and wash the original flask and the mineral wool with concentrated hydrochloric acid. The antimony is in the quinquevalent condition after boiling with the potassium chlorate.

Cool the solution to room temperature, or lower, and add 2 g. of potassium iodide and 1 c.c. of carbon tetrachloride. Titrate slowly with tenth-normal sodium thiosulfate solution until, after shaking, the violet color is no longer visible in the carbon tetrachloride. One cubic centimeter of tenth-normal $Na_2S_2O_3$ = 0.0060 g. of Sb.

The reactions that take place with the antimony throughout this analysis may be represented by the following equations.

$$3Sb + 15HCl + 5HNO_3 \rightarrow 3SbCl_5 + 5NO\uparrow + 10H_2O$$
$$SbCl_5 + 8KOH \rightarrow K_3SbO_4 + 5KCl + 4H_2O$$
$$2K_3SbO_4 + 3H_2C_2O_4 + 5H_2S \rightarrow 3K_2C_2O_4 + Sb_2S_5 + 8H_2O$$
$$Sb_2S_5 + 8HCl \rightarrow 2HSbCl_4 + 2S + 3H_2S$$
$$HSbCl_4 + 2KClO_3 + 3HCl \rightarrow SbCl_5 + 2KCl + 2ClO_2\uparrow + 2H_2O$$
$$SbCl_5 + 2KI \rightarrow SbCl_3 + 2KCl + I_2$$
$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Rapid Volumetric Analysis of Bearing Metal[1]

Determination of Lead.—Weigh 1 g. of alloy into a covered beaker containing 2 to 5 g. of tartaric acid and 10 c.c. of water. Add, while stirring, 10 c.c. of 7.5-normal nitric acid (concentrated acid with an equal volume of water) and heat below 60° until all of the alloy has dissolved. While heating on the water bath, add 2 or 3 drops of nitric acid if it seems necessary. A clear solution should be obtained. Add, while stirring, 5 c.c. of concentrated sulfuric acid diluted with an equal volume of water, and evaporate until no more nitrous fumes are evolved but not enough to cause charring of the tartaric acid. Cool, dilute to 100 c.c. and filter off the lead sulfate, washing with sulfuric acid diluted with 15 volumes of water. Place the lead sulfate precipitate and filter in a flask, add 10 c.c. of concentrated hydrochloric acid and boil until the filter is well disintegrated, then add 15 c.c. more of hydrochloric acid, 25 c.c. of cold water and 25 c.c. of strong ammonia. Introduce a few drops of litmus solution, add enough ammonia to make alkaline and then acetic acid to acid reaction. Heat to boiling and make sure that all of the lead sulfate is dissolved. Dilute to 200 c.c. with hot water and titrate with standard ammonium molybdate solution. At first reserve about one-third of the solution and add the molybdate until a drop of the solution on a porcelain "spot plate" gives a brown or yellow tinge when touched with a drop of 0.5 per cent tannin solution in water. This shows that the end-point has been passed. Add about half of the reserved solution and again titrate until the end-point is passed but use more care this time. Finally add the remaining solution to the contents of the flask and pour the solution back and forth from flask to beaker several times. Finish the titration by adding 2 drops at a time of ammonium molybdate. Watch the burette readings toward the last, estimate the value of 2 drops of the solution, and deduct it from the burette reading that corresponds to the first appearance of a yellow tinge.

The ammonium molybdate solution may be prepared by dissolving 4.74 g. of the solid in 1,000 c.c. Standardize against 0.2-g. portions of pure lead foil.

[1] This method of analysis is not recommended for precise work but an experienced operator can get good results with it.

Determination of Tin.—According to the tin content, weigh out 0.2 to 1.0 g. of alloy into a 350-c.c. Erlenmeyer flask and add 20 c.c. of concentrated hydrochloric acid. When most of the metal has dissolved add some potassium chlorate in small portions until all the alloy has dissolved. Boil off the chlorine, add 50 to 75 c.c. of concentrated hydrochloric acid, according to the probable antimony content, and dilute to 200 c.c.

Prepare a metal coil from a heavy sheet of nickel (1.5 by 4 in.) and place it in the flask, leaving a narrow strip of nickel attached to one side of the coil to reach above the top of the flask when the coil rests on the bottom. Bend this strip over the edge of the flask. Boil the solution gently for 3 min. to reduce any iron present, causing the yellow color to turn green. Remove from the hot plate and at once connect with a carbon dioxide generator. Pass carbon dioxide through the flask until the solution is cold. Remove the stopper from the flask and add two 0.5-in. cubes of calcite crystals. Remove the nickel coil and wash it with cold, 3-normal hydrochloric acid while withdrawing it. Add a little starch solution and titrate with tenth-normal iodine solution. One cubic centimeter of tenth-normal solution = 0.005935 g. of Sn.

Determination of Antimony.—Weigh 1 g. of the alloy into a 300-c.c. Kjeldahl digestion flask and heat with 10 to 15 c.c. of concentrated sulfuric acid until all the metal is dissolved and any sulfur that separates is volatilized. About 7 c.c. of concentrated acid should remain in the flask so that a hard salt cake will not form on cooling.

Cool, add slowly 20 c.c. of water and 20 c.c. of concentrated hydrochloric acid. Boil until certain that all the sulfur dioxide has been expelled. During this treatment any arsenic will be volatilized as trichloride but antimony will not.

Cool again, add water to a volume of 200 c.c. and adjust the hydrochloric acid concentration so that there is present 1 volume of concentrated acid to 10 of water for low antimony content and 1 to 5 for high antimony. Titrate the cold solution with tenth-normal potassium permanganate solution until 1 drop gives a color through the entire solution. The color soon disappears. One cubic centimeter of tenth-normal $KMnO_4$ = 0.0060 g. Sb.

Determination of Copper.—Dissolve 1 g. of alloy in 45 c.c. of concentrated hydrochloric acid and 5 c.c. of concentrated nitric acid. Boil down to 15 or 20 c.c. to remove all free chlorine. Wash down the sides of the flask and cover-glass with a little 6-normal hydrochloric acid from a wash bottle. Dilute to 75 c.c. and add 5 g. of tartaric acid dissolved in 20 c.c. of water. Make the solution alkaline with ammonium hydroxide and add hydrochloric acid until the blue color of copper-ammonia ions changes to green, showing that the solution is slightly acid. If necessary heat to dissolve lead chloride. Add 2 c.c. of stannous chloride solution (225 g. in 1,000 c.c. of 6-normal HCl) and 0.5 g. of potassium thiocyanate. Heat for a few minutes and filter off the white precipitate of cuprous thoicyanate. Wash with hot water until the excess thiocyanate is removed.

Place the filter and its contents in a 250-c.c. glass-stoppered bottle and, by means of a piece of moist filter paper, transfer into the bottle any precipitate that adheres to the beaker or stirring-rod. Add 5 c.c. of chloroform, 20 c.c. of water and 30 c.c. of concentrated hydrochloric acid. Titrate with standard potassium iodate solution until, on shaking, no blue color is seen in the chloroform.

The iodine is formed by the reaction:

$$2CuSCN + 3KIO_3 + 4HCl \rightarrow 2CuSO_4 + ICl + I_2 + 2HCN + H_2O + 3KCl$$

but disappears as soon as sufficient potassium iodate has been added

$$2I_2 + KIO_3 + 6HCl \rightarrow KCl + 5ICl + 3H_2O$$

The entire reaction is then:

$$4CuSCN + 7KIO_3 + 14\,HCl \rightarrow 4CuSO_4 + 7ICl + 4HCN + 7KCl + 5H_2O$$

A convenient strength for the standard potassium iodate solution is one-fifth gram-molecular-weight per liter. Such a solution is obtained by dissolving 42.80 g. of pure potassium iodate in water and diluting to exactly 1 liter in a calibrated flask. One cubic centimeter of such a solution = 0.007265 g. of Cu.

ARSENIC

The presence of a small quantity of arsenic has a serious effect upon the electrical conductivity of copper. The chemist, therefore, is often called upon to determine the arsenic content of copper and the method of analysis is applicable to any alloy.

By dissolving in hydroehloric acid in the presence of ferric ions, the arsenic is converted into arsenic trichloride[1] which distils off with hydrochloric acid. The distillate can be collected and, after neutralizing, the arsenic can be titrated with tenth-normal iodine solution. Since hydrochloric acid often contains a little arsenic it is necessary to run a blank test using all the details of manipulation as in the actual analysis.

DETERMINATION OF ARSENIC IN A COPPER ALLOY

Weigh 1 g. of the alloy into a distilling flask and add 10 c.c. of ferric chloride solution (d. 1.43) 60 c.c. of concentrated hydrochloric acid, 20 c.c. of water and 5 g. of solid potassium chloride. Connect the flask with a condenser and heat gently until the metal is all in solution. Then distil until only a little liquid remains in the flask, catching the distillate in a flask surrounded by ice. Add 50 c.c. more of hydrochloric acid and repeat the distillation.

To the cold distillate add 25 g. of solid sodium hydroxide in small pieces and finish the neutralization of the solution with sodium carbonate, being careful to keep the solution cold and to avoid loss by effervescence. Add the sodium carbonate until the solution is no longer acid to litmus then add 1 g. of sodium bicarbonate and a little fresh starch solution. Titrate with 0.02 normal iodine until a blue color is obtained One cubic centimeter of 0.02-normal iodine 0.00075 g. of As.

The reactions that take place in this analysis are as follows:

$$Cu + 2Fe^{+++} \rightarrow Cu^{++} + 2Fe^{++}$$

$$As + 3Fe^{+++} + 3HCl \rightarrow AsCl_3 + 3Fe^{++} + 3H^+$$

$$AsCl_3 + H_2O + 2Na_2CO_3 \rightarrow NaH_2AsO_3 + 3NaCl + 2CO_2 \uparrow$$

$$NaH_2AsO_3 + I_2 + 2NaHCO_3 \rightarrow NaH_2AsO_4 + 2NaI + 2CO_2 \uparrow + H_2O$$

As long as the solution is saturated with CO_2 there is no danger of NaIO being formed from sodium carbonate and iodine.

[1] Arsenic chloride boils at 132° and freezes at −18°. It distils with hydrochloric acid more readily than stannic chloride, boiling point 113.9°.

COPPER

This element constitutes the principle ingredient of most of the alloys mentioned in this chapter. It is one of the easiest metals to determine quantitatively; it is easily deposited electrolytically, forms several characteristic insoluble compounds which can be weighed with accuracy, can be titrated volumetrically in at least three different ways, and forms highly colored ions, particularly with ammonia. On p. 146 a rapid and accurate volumetric method was described. Chief emphasis will be placed here upon the method of attacking typical copper alloys, such as brass and bronze and three procedures for determining the element electrolytically and another well-known volumetric method will be described. The utility of the method must be considered as well as the accuracy; the electrolytic and volumetric methods for determining copper are easier to carry out and just as accurate as other methods which might be mentioned, such as the gravimetric determination as cupric oxide, cuprous sulfide or cuprous thiocyanate.

Brass is an alloy of copper and zinc but is likely to contain small quantities of other elements (*cf.* p. 307). If a clear solution in nitric acid is obtained which shows no turbidity on standing for some time in a warm place, it may be assumed that no tin is present. If a slight turbidity is formed it may be regarded as pure metastannic acid, but if a considerable precipitate results, the alloy is to be regarded as a bronze and the metastannic acid should be purified. The analysis of brass and bronze for tin will be considered at this place because it is advisable to remove tin before determining the copper and lead and small quantities of lead and copper are often found in the metastannic acid. Lead will be discussed because it is easy to determine lead and copper simultaneously.

ANALYSIS OF BRASS AND BRONZE[1]

Dissolving the Alloy.—Weigh 1 g. of alloy into a beaker of about 150-c.c. capacity. Cover the beaker with a watch-glass and add 10 c.c. of strong nitric acid. When the action has

[1] The methods given in this chapter are based for the most part upon the procedures recommended by the American Society for Testing Materials. The directions have been modified somewhat.

ceased, wash down the sides of the beaker and the cover glass, raise the latter by means of a glass triangle and evaporate the solution to dryness without boiling the solution or overheating the residue. Moisten the dry residue with 2 c.c. of 6-normal nitric acid and digest a short time near the edge of a hot plate. Add 50 c.c. of hot water, heat to boiling and keep the solution hot but not boiling for 1 hr. If there is any residue[1] filter the hot solution through a 7-cm. filter, containing some macerated filter-paper pulp, into an electrolyzing beaker of about 150-c.c. capacity and with relatively high sides and narrow cross-section.

Wash the precipitate with small portions of hot water until the washings are neutral to litmus. Carefully examine the filtrate and refilter if necessary. The first and last portions of filtrate are the most likely to show turbidity and for this reason it is best to collect the filtrate in a small beaker and transfer it to the electrolyzing beaker in portions found to be clear; in this way it will never be necessary to refilter the entire solution.

[1] The evaporation and digestion with nitric acid are necessary to remove the last traces of tin from the solution. Tin dissolves in dilute nitric acid to form stannous nitrate but the stannous ions are easily oxidized to the stannic condition and a gelatinous precipitate forms as a result of hydrolysis. The stannic acid remains in colloidal solution at first but tends to change into the hydrogele. The evaporation with nitric acid also causes precipitation of any silicon as silicic acid and it is sometimes doubtful whether a slight precipitate is silicic acid or metastannic acid; in the former case it may arise from silicon in the alloy or from the action of acid upon glass. Silicic acid can be distinguished from metastannic acid by heating with sulfuric and hydrofluoric acids in platinum. In alloy analysis, the use of platinum crucible is avoided as much as possible for heating precipitates, because a relatively small quantity of copper, lead or other reducible metal when ignited with filter paper is likely to spoil the crucible.

The last traces of tin are hard to precipitate as metastannic acid. Certain substances, particularly chlorides, exert a so-called *peptonizing* effect and convert the hydrogele to hydrosole.

The literature is full of conflicting statements concerning the purity of metastannic acid as obtained in alloy analysis. It is perfectly true that fairly pure precipitates are often obtained and that it is not always necessary to purify the precipitate. All colloids, however, show more or less tendency to adsorb certain substances in solution and the extent of the adsorption is greater in more concentrated solutions and the adsorption increases on standing. Arsenic acid and phosphoric acid are adsorbed to a marked degree by metastannic acid and iron, titanium, copper, lead, etc. are often found in the precipitate.

Determination of Tin.—Transfer the precipitated metastannic acid and filter paper to a weighed porcelain crucible. Heat carefully with a small flame at the mouth of the crucible until the paper is dry then place the flame at the base of the inclined crucible and heat with a low flame until the paper is all consumed without taking fire. Ignite strongly for 10 min., cool in the air until below 100° and then in a desiccator. When cold it is ready to weigh.

If the weight of stannic oxide corresponds to less than 2 per cent tin in the sample it may be regarded as pure, containing 78.80 per cent Sn. If more than 2 per cent of tin is present, the stannic oxide should be purified.

To purify the precipitate, add 10 times as much of a mixture of equal parts sodium carbonate and sulfur. Mix well, cover the crucible and heat with a low flame until the flame of burning sulfur is no longer visible around the edges of the cover. Cool and leach out the soluble sodium salts with hot water. The aqueous extract contains the tin as sodium thiostannate, together with sodium thioarsenate and sodium thioantimonate if arsenic and antimony are present. Traces of copper sulfide, and other sulfides, are dissolved by the excess of polysulfide formed during the fusion. Add a little sodium sulfite or thiosulfate until the deep brown color of the solution disappears and heat to coagulate the insoluble sulfides. Filter and wash thoroughly with hot water, using hydrogen sulfide water toward the last. Ignite the precipitate carefully in a weighed porcelain crucible and dissolve the oxide residue in a few drops of nitric acid. Add the resulting solution to the original nitric acid solution of the alloy. In case no phosphorus is present, the weight of these last oxides subtracted from the weight of the impure stannic oxide will give the weight of pure stannic oxide. This weight, however, may be determined by direct analysis as follows:

Add hydrochloric acid to the aqueous extract of the sodium carbonate fusion until slightly acid, saturate with hydrogen sulfide, heat to boiling and filter. Wash the precipitate of stannic sulfide with hot water until free from chloride and ignite carefully in a weighed porcelain crucible. Do not allow the paper or sulfur to take fire as there is danger of losing some stannic sulfide by volatilization or of forming some stannic sulfate;

the former error causes low results and high values result from the latter error. Finally heat over the Méker burner and weigh as stannic oxide, SnO_2.

The chemical reactions that take place in the analysis for tin may be expressed by the following equations:

$$3Sn + 4H^+ + 4NO_3^- + H_2O \rightarrow 3H_2SnO_3 + 4NO \uparrow$$
$$2SnO_2 + 9S + 2Na_2CO_3 \rightarrow 2Na_2SnS_3 + 3SO_2 + 2CO \uparrow$$
$$2CuO + 3S \rightarrow 2CuS + SO_2 \uparrow$$
$$Na_2SnS_3 + 2HCl \rightarrow 2NaCl + H_2S \uparrow + SnS_2$$
$$SnS_2 + 2O_2 \rightarrow SnO_2 + 2SO_2 \uparrow$$

Determination of Tin.—*Alternate Method.*—The American Society for Testing Materials recommends the following procedure: Dissolve 2 g. of alloy in 10 c.c. of concentrated hydrochloric acid and 5 c.c. of concentrated nitric acid. Dilute the solution to 75 c.c., add a slight excess of ammonium hydroxide, filter, wash the precipitate with dilute ammonium hydroxide and discard the filtrate. Dissolve the precipitate in hot dilute hydrochloric acid, dilute to 75 c.c. and again precipitate with ammonium hydroxide as before. Dissolve the precipitate in hot, dilute sulfuric acid and for the third time add ammonium hydroxide but stop when the solution is barely acid. Allow the solution to stand and if any lead sulfate forms, filter it off. Saturate the solution with hydrogen sulfide, heat to boiling, filter and wash the stannic sulfide precipitate with ammonium nitrate solution. Dry, ignite very carefully in a weighed porcelain crucible, and finally heat strongly and weigh, when the crucible is cold, as stannic oxide, SnO_2.

The reactions that take place in this method of analysis may be expressed as follows:

$$3Sn + 12HCl + 4HNO_3 \rightarrow 3SnCl_4 + 8H_2O + 4NO \uparrow$$
$$3Cu + 6HCl + 2HNO_3 \rightarrow 3CuCl_2 + 4H_2O + 2NO \uparrow$$
$$SnCl_4 + 4NH_4OH \rightarrow Sn(OH)_4 + 4NH_4Cl$$
$$Cu^{++} + 4NH_4OH \rightarrow Cu(NH_3)_4^{++} + 4H_2O$$
$$Sn(OH)_4 + 2H_2SO_4 \rightarrow Sn(SO_4)_2 + 4H_2O$$
$$Sn(SO_4)_2 + 2H_2S \rightarrow SnS_2 + H_2SO_4$$
$$SnS_2 + 3O_2 \rightarrow SnO_2 + 2SO_2$$

Method A. Determination of Lead and Copper.—This method depends upon the simultaneous deposition of dioxide upon the

anode and metallic copper upon the cathode by the electrolysis of a stirred nitric acid solution, obtained as described above.

Electrodes.—The cathode is made preferably of platinum gauze with about 400 meshes per square centimeter or 45 wires to the linear inch. It should be stiffened at the top and bottom by doubling the gauze or by welding it to a narrow band of platinum. The gauze should be made into a continuous cylinder about 30 mm. in diameter and 40 mm. tall. The stem should be made of 1.14 or 1.29-mm. wire and welded to the cylinder from top to bottom. Instead of the gauze electrode, any other of the well-known shapes of electrodes made of sheet platinum may be used but gauze electrodes are preferred because they permit greater diffusion of the electrolyte and there is less danger of obtaining spongy deposits.

The anode may be of the spiral type when less than 0.2 per cent of lead is present but a gauze electrode, about 12 mm. in diameter, is better. In brass analysis the anode should fit inside the cathode so that it can be rotated without danger of touching. In bronze analysis it is well to make the anode larger than the cathode because the lead dioxide does not adhere as well to the electrode as the copper does and for this reason the anode should not be rotated when the lead content is more than a few tenths of one per cent. In bronze analysis, therefore, it is better to rotate the cathode, if it is desired to stir the electrolyte so that considerable current can be used,[1] without the formation of spongy copper. This can be accomplished satisfactorily, as suggested by Gooch, by using a platinum crucible as cathode. The crucible is fastened to the negatively charged rotating shaft of the stirrer by means of a rubber stopper and electrical connection made by means of a wire pressing against the crucible and attached to the shaft. Deposits adhere better to sand-blasted electrodes than to polished ones.

Procedure.—Use as electrolyzing beaker one that is just large enough to hold the electrodes conveniently, so that not over 100 c.c. of solution suffice to wet at least three-quarters of the electrode surface. Before placing the weighed electrodes in the beaker, make all the electrical connections and be sure that

[1] With stationary plate electrodes, a current of about 0.2 ampere will give satisfactory results in about 20 hr .

the electrode to be rotated is properly centered. Adjust the beaker support so that the stationary electrode touches the bottom of the beaker. The electrolyte should not exceed 100 c.c. in volume and is obtained as described on page 320.

With the current turned off, and the electrodes and beaker in place, start the stirrer to make sure that there will be no spattering when it revolves at a rate of 600 to 900 r.p.m. Turn on about 3 amperes of current and note the time. When the solution has become colorless, add about 0.1 g. of urea and, if there is marked effervescence produced, carefully add enough more urea to decompose all the nitrous acid, which prevents complete deposition of copper. Reduce the current to about 1 ampere and electrolyze 10 min. longer. Then wash down the sides of the beaker and note whether there is any further deposition of copper upon the freshly wetted surface after 5 min.

When convinced that all the copper has been deposited, start removing the beaker, without turning off the current, and wash both electrodes while withdrawing the beaker. Then turn off the current and promptly rinse the electrodes with water and give them two baths with 95 per cent alcohol. Dry the anode at 180 to 210° for 30 min. and weigh as PbO_2. Dry the cathode at 110°, watching it as it dries, and remove as soon as no more dampness is visible.[1] Cool and weigh.

Test the solution for copper by making it ammoniacal. If any sign of blue color is obtained, acidify with dilute sulfuric acid and electrolyze some more with clean electrodes.

NOTES.—The results of the lead determination are likely to be a little high as the deposit tenaciously retains a little moisture. The error from this source can be disregarded in the analysis of brass and bronze.

The reactions that take place in the determination of lead and copper in brass and bronze may be expressed as follows, using ⊖ to represent a unit charge of negative electricity:

$$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{++} + 2NO\uparrow + 4H_2O$$

$$3Pb + 2NO_3^- + 8H^+ \rightarrow 3Pb^{++} + 2NO\uparrow + 4H_2O$$

$$Cu^{++} + 2\ominus \rightarrow Cu$$

$$Pb^{++} + 2H_2O - 2\ominus \rightarrow PbO_2 + 4H^+$$

[1] The excess of alcohol may be shaken off and the electrode dried by burning the alcohol that remains. Unless the electrode is kept in motion this will cause oxidation of a little copper and a black stain of oxide will result.

As explained on page 265, 96,500 coulombs = 96,500 ampere-seconds are required to deposit 31.8 g. of copper, or 1 ampere-second will deposit 0.328 mg. copper. To precipitate 0.7 g. of copper, which corresponds to the copper content of 1 g. of good cartridge brass, a current of 3 amperes would require about 12 min. if the current is utilized entirely for depositing copper.

As mentioned on p. 266, the copper is harder to deposit as the concentration falls and stirring helps to bring copper ions into contact with the cathode. With gauze electrodes in a small beaker, there is more diffusion throughout the electrolyte than when the electrodes are solid plates in a dilute solution and the passage of a fairly strong current causes heating which starts convection currents. It is inevitable, however, that the discharge potential of some other ion in solution will be reached before the last trace of copper is deposited. Next to copper the two ions most likely to be discharged at the cathode in an acid solution are hydrogen ions and nitrate ions:

$$2H^+ + 2\textcircled{e} \rightarrow H \qquad (1)$$

$$NO_3^- + 10H^+ + 8\textcircled{e} \rightarrow NH_4^+ + 3H_2O \qquad (2)$$

$$NO_3^- + 2H^+ + 2\textcircled{e} \rightarrow NO_2^- + H_2O \qquad (3)$$

The discharge of hydrogen ions together with copper is the cause of spongy deposits. If the reduction of the nitrate ion takes place to form an appreciable quantity of nitrous acid, the further deposition of copper is prevented and in many cases the copper begins to dissolve. The purpose of adding urea is to decompose nitrous acid[1] but under the conditions recommended there is not much formed unless too much current is used. The reduction of the nitrate ion may cause lessening of the acidity as equation (2) shows;[2] eventually the solution becomes neutral and then zinc will precipitate. Many chemists prefer to electrolyze sulfuric acid solutions because there is not this danger of the solution becoming neutral if nitrate ions are absent but, on the other hand, ammonium nitrate is often added to prevent the formation of spongy copper. If the nitric acid is absolutely

[1] $CO(NH_2) + 2HNO_2 \rightarrow 2N_2 \uparrow + CO_2 \uparrow + 3H_2O$.

[2] Equations (1) and (3) do not cause loss of acidity because H^+ ions are being formed at the anode in equal amount to those removed at the cathode.

$2H_2O - 4\textcircled{e} \rightarrow 4H^+ + O_2$.

free from nitrous acid, it does not dissolve copper. A little nitrous acid is likely to be present and when the reaction between copper and nitrous acid takes place, more nitrous acid is formed so that it is not safe to leave the deposit in contact with the solution when the current is turned off.

$$2NO_2^- + Cu + 4H^+ \rightarrow Cu^{++} + 2NO + 2H_2O$$
$$2NO + NO_3^- + H_2O \rightleftarrows 3NO_2^- + 2H^+$$

Method B. Electrolysis with Stationary Electrolyte.—In this method, which is advocated by the American Society for Testing Materials, the solution is kept hot which serves to hasten the electrolysis, partly by changing the resistance of the electrolyte and partly by causing diffusion currents to stir up the solution. In the hot solution there is also less danger of a little manganese dioxide deposit forming on the anode. Use as electrodes a pair of sand-blasted, gauze electrodes of the size recommended on page 323. To the solution obtained as described on page 320, add enough nitric acid to make it contain 10 per cent by weight. This is easy to estimate because the acid in 1 c.c. of 15-normal nitric acid (d. 1.42) weighs nearly 1 g. Heat the solution to boiling and boil very gently for 1 min. to remove nitrous acid. Then electrolyze the hot solution at a volume of about 100 c.c. with a current of 3 to 5 amperes and approximately 10 volts between the electrodes. After about 45 min. the lead will have been completely deposited and the concentration of the nitric acid will have been reduced materially by cathodic reduction, as explained under Method *A*. The presence of nitric acid favors the deposition of the lead as dioxide upon the anode but too much nitric acid was added to permit the complete deposition of the copper in this time. Add 3 c.c. of concentrated sulfuric acid and electrolyze until the solution is colorless. Wash down the cover glass, electrodes and sides of the beaker and see if any more copper is deposited. When the electrolysis is finished remove the electrodes as described in Method *A*.

NOTES.—Considerable phosphoric, arsenic, telluric and selenic acids will prevent the deposition of lead as dioxide but there is never enough of these elements found in brass or bronze to cause errors of this nature.

The deposited copper is dissolved off the electrode without difficulty by warming with 3-normal nitric acid. A slight deposit of lead dioxide will dissolve in this acid but it dissolves more rapidly if a little hydrogen peroxide, or oxalic acid, is added to the nitric acid solution.

Manganese and bismuth are the only other common metals likely to deposit upon the anode. To test the anode deposit for bismuth and manganese, dissolve it in nitric acid with a few drops of hydrogen peroxide. Add 2 c.c. of concentrated sulfuric acid and evaporate to fumes. Cool, pour into 25 c.c. of cold water and allow the lead sulfate precipitate to settle. Filter and apply the usual qualitative tests for bismuth and manganese.

Method C. Removal of Lead as Sulfate and Determination of the Copper by Electrolysis or by the Iodide Method.—Dissolve 5 g. of the alloy in 25 c.c. of concentrated nitric acid and precipitate any tin as metastannic acid by evaporating to dryness. Add 16 c.c. of concentrated nitric acid to the residue and digest a short time at 90°. Add 85 c.c. of hot water and boil gently for a few minutes. Filter off the metastannic acid as described on page 320 and after adding 10 c.c. of concentrated sulfuric acid evaporate the filtrate till copious fumes are evolved. Cool, pour into 50 c.c. of cold water, boil to dissolve all the copper sulfate, cool and allow the lead sulfate to settle at least 5 hr.

Filter off the precipitate into a properly prepared and weighed Gooch crucible[1] and wash with 5-c.c. portions of 5 per cent sulfuric acid. Remove the filtrate and finish washing with a little 50 per cent alcohol. Place the Gooch crucible in a larger porcelain crucible, dry carefully and finally heat 5 min. with the full heat of a Tirrill burner. Cool and weigh as lead sulfate containing 68.29 per cent lead.

Or, instead of determining the lead as sulfate, it may be collected upon a paper filter and dissolved in a hot ammonium acetate solution (1 vol. concentrated ammonia: 1 vol. water: enough 80 per cent acetic acid to make the solution barely acid). Rinse the precipitate into a small beaker by a stream of hot water from the wash bottle and dissolve the part that adheres to the filter by pouring small portions of the ammonium acetate solution through the filter, followed by a little hot water, until a portion of

[1] It must have been heated as in the analysis.

the filtrate gives no blackening with ammonium sulfide solution. It is well to use as little ammonium acetate as possible because it exerts a slight solvent effect upon the lead chromate. Dilute the solution to 50 c.c. and add just enough saturated potassium dichromate solution to color it. Heat to coagulate the precipitate, filter into a properly prepared Gooch crucible, wash with water and dilute alcohol, dry at 110° for an hour and weigh. Calculate the lead on the assumption that the precipitate contains 63.75 per cent lead.

A precipitate of lead sulfate which can hardly be seen will give a characteristic lead chromate precipitate.

Transfer the sulfuric acid solution from which the lead has been removed, to a 500-c.c. calibrated flask. Make up to the mark at room temperature, mix thoroughly and pipette off 50 c.c. of the solution for the determination of copper, zinc, etc.

The copper may be determined in either of the following ways: (1) Add 1 g. of solid ammonium nitrate and electrolyze as in Method A. (2) Titrate with sodium thiosulfate as described below:

Iodometric Determination of Copper in Alloys. This method can be applied directly to the analysis of such metals as brass, bronze and German silver and is accurate.

Procedure.—Dissolve 0.5 g. of alloy in a 250-c.c. flask with about 10 c.c. of aqua regia. Boil off the excess acid by heating over a low flame but keeping the flask in constant motion. Dilute with water to about 50 c.c. and add sodium carbonate solution until nearly neutral and a blue precipitate of basic copper carbonate is obtained. Dissolve the precipitate in a slight excess of acetic acid and boil to expel carbonic acid. If a precipitate of basic ferric acetate forms, remove it by filtration and wash with hot water. Cool to room temperature, add 3 g. of solid potassium iodide. Shake and after 2 min. titrate with sodium thiosulfate solution until the mixture is faintly yellow. Then add a little fresh starch solution and titrate until the deep blue color disappears and a pink precipitate of cuprous iodide remains (*cf.* p. 147).

One cubic centimeter of tenth-normal sodium thiosulfate solution = 0.00636 g. Cu.

IRON

Proceed as in the analysis for tin, page 322. Take the filtrate from the tin sulfide precipitate, boil off hydrogen sulfide and oxidize by adding a little bromine water. Add a slight excess of ammonium hydroxide, heat to boiling and filter. The precipitate will contain any iron as hydroxide and possibly other hydroxides which will not interfere with the iron determination. Dissolve the precipitate on the filter with a little hot, dilute hydrochloric acid. A good way is to first moisten the precipitate with hot water, pour about 2 c.c. of 3-normal hydrochloric acid upon it, and wash down with a stream of hot water, catching the filtrate in a small beaker. Repeat the treatment until the ferric hydroxide is all dissolved but do not use more than 10 c.c. of 6-normal hydrochloric acid. There should be no yellow stain of ferric chloride remaining on the filter. Heat the solution to boiling, reduce with stannous chloride and titrate as described on page 232.

LEAD

The analysis of typical lead alloys has been discussed on page 312 and on page 322.

MANGANESE

The principles upon which various methods of determining manganese in alloys depend have been explained in Chaps. III and XXI. The following procedures are suitable for the analysis of commercial non-ferrous manganese alloys in which the manganese content is low.

Persulfate Method.—Dissolve 1 g. of alloy, or proportionately less if more than 0.15 per cent of manganese is present, in a mixture of 5 c.c. concentrated sulfuric acid, 2 c.c. concentrated nitric acid and 17 c.c. water. Heat until the alloy is dissolved and expel oxides of nitrogen. Add 2 c.c. of tenth-normal silver nitrate solution and 20 c.c. of 6 per cent ammonium persulfate solution. Let the solution heat on the water bath until a good permanganate color results and no gas bubbles are seen to rise when the solution in the flask is given a whirling motion. Cool to below 25°, add 50 c.c. of cold water and titrate with approximately 0.06-normal sodium arsenite solution.

Prepare the sodium arsenite solution by dissolving 4.3 g. of arsenious oxide with 10 g. sodium carbonate and 30 c.c. of water. Filter if necessary and dilute to 2000 c.c. with water. One cubic centimeter of this solution will equal approximately 0.0005 g. of manganese.

Standardize the sodium arsenite solution against pure manganous sulfate crystals obtained by drying the pure crystals at about 200°; the anhydrous salt contains 36.38 per cent Mn. Weigh out about 2 g. of the manganous salt into a 100-c.c. calibrated flask, dissolve in a little water, make up to the mark and mix thoroughly by pouring back and forth into a dry beaker. Withdraw 10-c.c. portions, by burette or pipette, for the standardization and proceed exactly as in the analysis of the alloy.

Bismuthate Method.—Dissolve 1.5 g. of alloy in 50 c.c. of 25 per cent nitric acid (*cf.* p. 50 and p. 286). Without filtering, add about 0.5 g. of bismuthate and heat until the purple color of permanganate disappears. If a precipitate of manganese dioxide is obtained, add a little pure ferrous salt to dissolve it and boil until oxides of nitrogen are expelled. Cool to at least 20° and add a slight excess of sodium bismuthate. Filter as described on page 52 and titrate the manganese as described there.

NICKEL

Dissolve not more than 0.5 g. of drillings in 10 c.c. of 6-normal nitric acid. Filter if necessary. Add 40 c.c. of water, 1 g. of tartaric acid and ammonia until a deep blue color of copper-ammonia ions is obtained. Heat to about 50°, add an excess of 1 per cent dimethylglyoxime solution and finish the analysis as described on p. 177.

PHOSPHORUS

Dissolve 1 g. of alloy in 10 c.c. of concentrated nitric acid in a 300-c.c. casserole. Add 20 c.c. of concentrated hydrochloric acid and evaporate to dryness. Moisten the residue with hydrochloric acid and add 3 c.c. of ferric chloride solution (100 g. $FeCl_3$ in 100 c.c. water). Dilute to about 200 c.c., add ammon-

ium hydroxide until the basic copper salt is all dissolved and then boil. Allow the precipitate of ferric hydroxide and phosphate (and arsenate if arsenic is present) to settle, filter and wash with dilute ammonia and water. Dissolve the precipitate in hot, dilute hydrochloric acid, dilute to 200 c.c. and add ammonia until the precipitate that forms where the ammonia comes in contact with the solution dissolves very slowly and saturate with hydrogen sulfide. Heat to coagulate the precipitate, filter and reject it. Boil the solution to expel hydrogen sulfide, add concentrated nitric acid until the iron is all oxidized and again precipitate with ammonia, washing as before. Dissolve this precipitate in 6-normal *nitric* acid and receive the filtrate in a 300-c.c. Erlenmeyer flask. Add ammonia until the iron is all precipitated and then just enough concentrated nitric acid to clear up the solution. Heat to 80°, and add 40 c.c. of ammonium molybdate solution. Allow the solution to stand 1 min., shake for 3 min. and finish the analysis as in the analysis of iron and steel. (See Chap. IV.)

TIN

See pp. 321 and 322.

ZINC

The zinc content of brass and bronze is often determined "by difference," *i.e.* by subtracting all of the other values obtained from 100 per cent. This is justifiable in many cases of commercial testing but the practice is a dangerous one. If any error has been made in the previous work, it may escape detection.

In commercial work the volumetric method depending upon the titration of zinc ions, after the removal of most other cations, with ferrocyanide ions is much used. The method is a good one and can be applied without difficulty to the solution from which the copper and lead have been removed by electrolysis. The titration is made with standard potassium ferrocyanide solution in a solution heated to at least 60° and the end-point is commonly determined by touching with uranium solution on a spot plate. The operator has to practice a little before he learns is to distinguish the true end-point and the method, therefore, to be recommended only for persons who are experienced and such chemists will not need directions here.

The electrolytic determination of zinc is also satisfactory but unless particular pains are taken the results are likely to be a little high owing to oxidation. From the position of zinc in the electrochemical series, it might be argued that this metal could not be deposited upon the cathode in the presence of free acid. It can however, be deposited from acetic acid solutions containing sodium acetate, because of the overvoltage that zinc shows toward the discharge of hydrogen.

The gravimetric determination of zinc after precipitation as zinc ammonium phosphate is, all things considered, the most satisfactory method for determining zinc and a beginner can follow the directions and get accurate results. For this reason it will be the only method described.

The sole difficulty with regard to the determination lies in the fact that nearly all other metals, except the alkalies, form insoluble phosphates. Most of these phosphates, except those of copper, cadmium, zinc, nickel and cobalt, are insoluble in an excess of ammonium hydroxide.

Fortunately, in the analysis of bronze and brass it is often safe to assume that none of these elements are present, when it comes to the determination of zinc.

The qualitative separation of zinc and cadmium is usually accomplished by introducing hydrogen sulfide into 0.3-normal hydrochloric acid solution. If, however, a large quantity of zinc is present and a small quantity of cadmium, the separation is imperfect. It is best to reduce the acid concentration so that some of the zinc precipitates. By dissolving the precipitate in hot hydrochloric acid, diluting and repeating the precipitation twice more with hydrogen sulfide in approximately 2-normal acid solution, it is possible to detect a trace of cadmium in every zinc alloy provided a large sample of the metal is taken for analysis. Copper should be absent during this treatment, although its sulfide will not dissolve appreciably in the hot hydrochloric acid and is merely troublesome. It is rarely necessary, however, to determine the cadmium content as the quantity usually present in alloys is insignificant. A cadmium sulfide precipitate can be converted to sulfate by sulfuric acid and weighed as such in a porcelain crucible.

The separation of zinc from iron, nickel, cobalt, manganese and

ions of the alkaline earth group can also be accomplished by means of hydrogen sulfide, Make the solution left after the determination of copper by electrolysis, alkaline with ammonium hydroxide, add enough 40 per cent formic acid to make the solution neutral and leave 5 c.c. in excess, heat the solution to boiling and precipitate the zinc in a volume of about 300 c.c. Filter and wash with hot water containing hydrogen sulfide. Zinc sulfide precipitates are often hard to filter and are bulky. By careful roasting in a porcelain crucible the zinc can be converted to oxide and weighed as such; this method is suitable when the zinc content is low. With considerable zinc, it is better to dissolve the precipitate in hydrochloric acid and precipitate as zinc ammonium phosphate.

It is a matter of indifference whether the zinc ammonium phosphate is weighed as such, after drying at 120 to 130° or whether it is ignited carefully in a weighed porcelain crucible and weighed as zinc pyrophosphate, $Zn_2P_2O_7$.

In precipitating zinc as phosphate it is important to remember that zinc ammonium phosphate dissolves easily in dilute hydrochloric acid and in dilute ammonia solution. In the former case, very slightly ionized HPO_4^{--} is formed and in the latter case very slightly ionized zinc ammonia ions, $Zn(NH_3)_4^{++}$ or $(Zn(NH_3)_6)^{++}$.

Procedure.—Treat the cold, acid solution obtained after the removal of the copper and lead by electrolysis, or, by the dissolving of zinc sulfide in hydrochloric acid, if it is thought necessary to go through the above-described purification, with dilute ammonium hydroxide solution until it is left barely acid to litmus. Care is necessary at this point. Dilute, if necessary, to about 150 c.c. and heat on the water bath. To the hot solution, add 10 times as much diammonium phosphate as there is zinc present. (If there is some monoammonium phosphate in the salt, it should be dissolved in a little cold water and treated with ammonium hydroxide solution until it is barely ammoniacal to phenolphthalein). The precipitate is amorphous at first but becomes crystalline very quickly, when heated on the water bath. The transformation takes place more rapidly in proportion to the amount of ammonium salts present and it is well to add 2 or 3 g. of ammonium chloride. After heating about 15 min. remove the beaker from the bath and allow the precipitate to settle for

a few minutes. Filter the solution through a weighed Gooch crucible and wash the precipitate 8 times with small portions of 1 per cent ammonium phosphate solution, twice with cold water, and once with 50 per cent alcohol. Dry at 120 to 130° for 1 hr. and weigh as $ZnNH_4PO_4$ containing 36.34 per cent zinc.

PART II

THE APPLICATION OF METALLOGRAPHY

TO THE

INSPECTION AND SAMPLING OF ALLOYS

CHAPTER XXIII

PREPARATION AND EXAMINATION OF THE SPECIMEN

The ultimate test of the quality of a metal is its behavior in actual service, or at least under conditions which approximate those to which it will be subjected in use. Such a test is necessarily expensive and time-consuming, and can only be resorted to in those special cases where absolute knowledge of the properties of the material outweighs all other considerations. In ordinary practice, shorter and cheaper tests must be used. The modern study of metals has shown that while the chemical composition of an alloy may be satisfactory, the metal due to improper heat treatment, mechanical treatment or both may be wholly unsuited for use. After a satisfactory chemical analysis of the sample has been made there are two additional questions to answer. (1) **Does the sample truly represent the material under examination?** (2) **Does the chemical analysis give all the needed information?**

With regard to the first question, if the material contains segregated areas, as for example a bar of steel with areas rich in phosphorus, a sample taken at random might represent either a high-phosphorus or a low-phosphorus area, and the chemical analysis may be of little value regardless of its correctness. The analyst can be held responsible only for the accuracy of his methods, unless the operation of sampling is placed under his control.

The second question may be illustrated by a reference to spring brass, whose hardness is produced by mechanical working of the cold metal. Hardness or brittleness, caused by such mechanical operations as rolling, hammering or drawing, cannot be detected by chemical analysis, consequently a material of excellent chemical composition may be wholly unsuited for a given purpose because of its mechanical condition.

It is the purpose of these chapters dealing, for the most part, with the microscopic examination of metals, to consider the

methods of metallography as they may be applied in answering the two fundamental questions just considered.

It is not possible to consider the subject of general metallography[1] here, but those phases of it which are of direct application to the microscopic study of the technical alloys are discussed briefly.

The microscope has proved itself of great and constantly increasing usefulness, not only as an aid in getting representative samples but also as a source of additional information concerning the properties of the metal under test. No attempt is made to separate these two uses of the microscope, as the general character of the metal determines whether or not special precautions are necessary in selecting representative samples for analysis. Microscopic study of alloys involves several factors; preparation of a suitably polished surface, development of the internal structure by means of chemical "etching reagents" or in some other way, the arrangement and use of the microscope in the examination of metals and finally an interpretation of the observations, usually with reference to the equilibrium diagram (p. 356).

Preparation of the Specimen.—If the specimen to be examined is a large one, as for example a broken rail, it is often advantageous to make an examination of a roughly polished surface without the microscope (macroscopic examination) in order to determine the particular areas which need more careful study.[2] When the suspected areas have been located, portions of the metal are sawed off at these places, the size of the specimen being determined by the nature of the material.

When a sample has been selected, the specimen is prepared for microscopic examination by rubbing one or more surfaces on a series of abrasive materials, each one finer than the one which precedes it, until a scratch-free, mirror surface is obtained. The exact sequence of abrasives is determined to some extent by the nature of the material to be examined, but the general method is

[1] For details of general metallography the reader is referred to DESCH, *Metallography;* GULLIVER, *Metallic Alloys;* ROSENHAIN, *Physical Metallurgy;* SAUVEUR, *Metallography and Heat Treatment of Iron and Steel;* WILLIAMS, *Principles of Metallography.*

[2] Details of "macroscopic examination" are given on p. 373.

as follows. If the material is hard, like steel, grind the surface first on a medium emery or carborundum wheel and then on a fine one taking pains to hold the specimen in such a way that the scratches produced by the first wheel will be eliminated by the action of the second. If the sample is moderately soft, like brass or Babbitt metal, clamp the specimen in a vise and file the surface flat using first a medium and then a fine file. The direction of filing with the fine file should be at right angles to that of the coarse file and the operation should be continued until the coarse file marks have been removed. **It is a general rule that when a specimen is being polished with a series of abrasives the direction of polishing with each abrasive should be at approximately right angles to that of the one next preceding it and that the polishing should be continued with each abrasive until the marks produced by the next coarser material have been wholly eradicated.**

After a fairly smooth surface has been obtained by grinding or filing, continue the polishing operation by rubbing the surface on a succession of emery cloths or papers, each one finer than the one before it. Many kinds of emery cloth and paper are available, but the most satisfactory for metallographic purposes is the French emery paper (Marke Hubert). If French emery paper is used, transfer the ground or filed specimen to the grade 1C, next to 1F and finally to 0 and 00. For special work with very soft alloys, the finer grades 000 and 0000 must be used and, in such a case, either the specimen or the emery paper must be kept moist with a light machine oil to get a satisfactory surface.

After as good a surface as possible has been obtained with the emery papers, continue the polishing operation by rubbing the specimen on cloths which have been treated with fine abrasive powders, applied to them in the form of suspensions in water or other suitable liquid. Polishing powders of this sort may be obtained from any dealer in metallographic or chemical supplies. An excellent series of abrasives for this special use, consisting of various grades of alundum with "levigated alumina" as the final polishing medium, has been prepared by the Norton Company of Worcester, Massachusetts. Rouge is often used and recommended by metallographers as the finest polishing powder, but although it gives a brilliant polish, it has a tendency to

cause a surface flow of the metal, and it is also a rather dirty material to handle.

The cloth, on which the suspension of polishing powder is sprayed or sprinkled, must be so soft that it will not itself scratch the softest metal. "Selvyt" is often recommended but the less expensive broadcloth known as "Lady Cloth" is satisfactory. The finest quality of chamois leather has been used also. When the polishing is to be done by hand, the cloths and emery papers are tacked to smooth boards about 3 by 8 in., often with a sheet of plate glass between the cloth and the board backing to insure an absolutely smooth surface. Machine

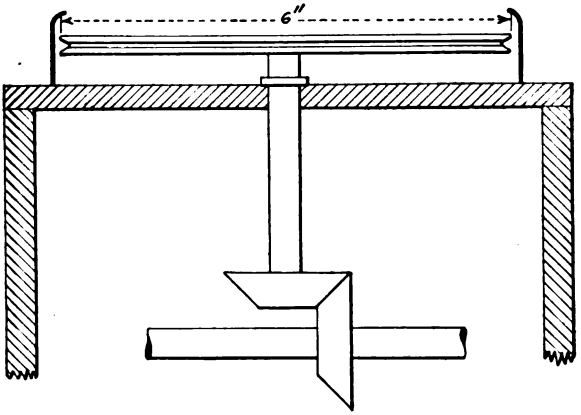


FIG. 46.—Section of polishing wheel.

polishing is much more rapid and efficient, and many excellent polishing machines of various types are now on the market. Most of them consist of disks rotating either in a vertical or in a horizontal position, a few consist of boards which move back and forth in a horizontal position and to which the polishing cloth or paper is attached. One modern type is composed of series of interchangeable cloth endless belts which move over horizontal cylinders and carry the different polishing substances. If power is available in the testing laboratory, it is a simple matter to build a polishing machine in the way indicated in the sketch, Fig. 46. The disks are made of wood or brass and are provided with a large groove in the outer edge, so that the tightly stretched cloth can be held in place by a band of wire or

by means of a strong elastic band or spiral spring. The wheels are guarded by cast-iron or sheet-steel cases to prevent the liquid polishing materials from being thrown out by the rotating wheel. The disks are 5 or 6 in. in diameter, and should rotate at about 300 r.p.m. **Every possible precaution should be taken to prevent the transfer of coarse polishing powder to a wheel to be used for fine material.** A single grain of coarse material on the final wheel may necessitate the repolishing of an otherwise perfect specimen. Suspended abrasives may be applied to the polishing disks by means of an ordinary wash bottle, be blown against the surface by an atomizer or be shaken on the surface by means of the simple shaking bottle shown in Fig. 47. The number of abrasive powders to be used depends on the hardness of the specimen to be polished, but for most technical alloys a satisfactory surface may be obtained with three; "60-min." emery, followed by "alundum F" and finally by levigated alumina. With very hard specimens one or two intermediate grades may be found necessary.

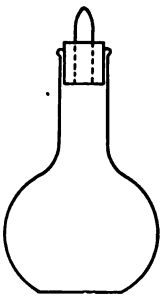


FIG. 47.—Flask for suspended abrasives.

Etching.—A highly polished metal surface has little or no characteristic structure under the microscope, unless it happens to be composed of two or more metals which do not mix in the solid state and which differ in color, or unless it contains slag or other non-metallic impurities. It is necessary, therefore, to treat the polished surface in such a way that the different constituents of the alloy are colored differently, or that one constituent is more rapidly dissolved than the other, producing a surface which is no longer smooth but covered with ridges and depressions, or in some way producing a contrast between the components, of the metal. This operation is called "etching" and is usually a selective chemical action. The particular reagent to be used to develop the surface structure depends on the composition and physical characteristics of the alloy under examination. Although a large number of reagents have been used for various purposes,[1] the study of the industrial alloys

[1] Cf. *Zeitshrift für Metallkunde*, **8**, 228 (1916).

requires only a small number of solutions. Dilute acids or alkalis are often used for general purposes, the particular reagent depending on the solubility of the constituents of the alloy to be studied. A solution of 10 g. of ferric chloride ($FeCl_3$) in 100 c.c. of alcohol is a useful reagent for many of the non-ferrous alloys. The special reagents which are commonly used in the examination of steels, brasses, bronzes and Babbitt metal are described in connection with the discussion of these important industrial alloys.

The Microscope.—For the examination of polished and etched metal specimens, a type of microscope is needed, with which the specimen may be examined by reflected instead of transmitted light. A " vertical illuminator," the principle of which is shown in the following sketch (Fig. 48) can be obtained from any dealer in optical apparatus at a moderate expense and may be fitted to an ordinary microscope. The source of light may be a small arc, a nitrogen-filled tungsten incandescent lamp or any other lamp giving a brilliant illumination which can be concentrated by means of a condensing lens. An outfit of this type is quite satisfactory for most of the microscopic work of a small laboratory and can be assembled at a small cost. If much microscopic work is to be done and especially if a photographic record is to be kept, one of the many excellent photomicrographic cameras will be found indispensable. All are alike in principle and consist of a train of lenses and mirrors, so arranged that a magnified image of an illuminated spot on the polished metal surface is transmitted either to the observer's eye for immediate examination or to a photographic plate for permanent record. The following standard magnifications for use in examining metals and in the preparation of photomicrographs have been adopted by the American Society for Testing Materials:

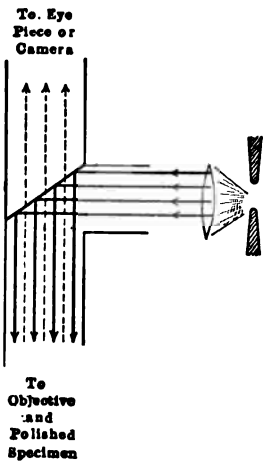


FIG. 48.—Sketch of vertical illuminator (sheet glass type) dotted lines show the direction of rays reflected from the specimen.

10, 25, 50, 75, 100, 200, 500, and **1,000** diameters[1]

See p. 464 for magnifications used in studying grain size.

The magnifications indicated represent the actual magnification of the image as recorded on the photographic plate, and the general adoption of these values would be of great help in comparing the results obtained by different observers on metals of the same class.

For the general examination of large areas on a specimen, rather than the detailed examination of a small area, a microscope like that shown in Fig. 49 is useful. Several instruments of this sort are on the market.

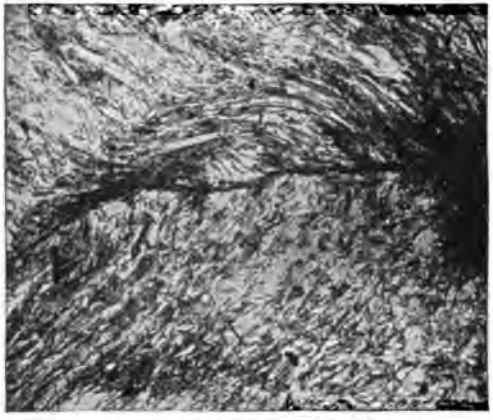
FIG. 49.—Low-powered microscope for examination of large areas.

Photographing the Specimen.—If, as is often the case, a permanent record of the defective material is to be kept, the metal-microscope is provided with a photographic attachment. The actual operation of taking the picture depends on the mechanical construction of the particular instrument used, so that details cannot be given here, but the process is not difficult and may be learned with very little practice. The plates used for the purpose must be fine grained, and for the brasses and bronzes must be color sensitive. "Wellington Ortho Process Plates" have been found satisfactory for all purposes, but for the photography of steel specimens, where color sensitiveness is of minor importance, the much less expensive "Stanley" plates may be used. Other plates which have been used successfully for photomicrographic work are the "Wratten M," "Standard Orthonon," "Cramer

Contrast" and "Imperial Standard." Any one of the standard process plates would no doubt be found satisfactory for the purpose. When colored alloys like brass and bronze are photographed, it is usually necessary to use a color screen in order to produce the needed contrast. A yellowish-green screen gives good results with the copper alloys, though some operators prefer a deep orange or even a red screen for the purpose. The screen is held in position between the source of light and the vertical illuminator. The time of exposure of the plate varies from a few seconds, with the unscreened light from an arc lamp, to 30 min. or more, with a less powerful light source and a deeply colored screen, and can only be determined by experience. Certain of the modern metallographic cameras are provided with an automatic plate holder by means of which a series of exposures of different lengths may be made on a single plate. After development the most suitable exposure time can be selected from the series so that later photographs taken under similar conditions can then be correctly exposed. If such an automatic device is not available, the same information can be obtained in the following way: Expose the plate as usual for a short interval, then push in the opaque slide, which is used to cover the plate in its holder, about ½ in. in order to shut off a portion of the exposed plate. Make a second exposure and push the slide in again another short distance. Repeat the operation, shutting off about a ½-in. strip of the plate each time from the action of the light, until the opaque screen has been returned to its final position in the holder. Develop the exposed plate and a series of bands will be found each of which represents a longer exposure than the one next to it, and from the time required to produce the band which shows the best detail, estimate the suitable exposure time for specimens of the same general character using plates of the same speed.

Photomicrographs should be printed on glossy paper in order to bring out the fine details of the structure. Glossy Velox, Glossy Cyko or other papers of the same type are commonly used and the best results are obtained if the prints are dried on a ferrotype plate. Unless special precautions are taken in the preparation of the ferrotype plate for use, much annoyance will be caused by the sticking of the prints to the polished surface. The usual

NUMBER 691



75 X

YIELD POINT	LBS./SQ.IN.	C	
TENSILE STRENGTH	LBS./SQ.IN.	MN	
ELONGATION	% CONTRACTION %	P	
HARDNESS		SI	
		S	
Cold worked brass showing crystal distortion and a crack due to overstrain .		NI	
		CR	
		W	
		V	
		CU	69.8
		ZN	30.0
ETCHED WITH NH_4OH and H_2O_2			
SECTION			

MATERIAL Cartridge brass.

FROM Thomas Smith Company.

FIG. 50.—Mounting card for photomicrograph.

causes of the difficulty are incompletely washed prints or an insufficiently polished surface of the plate. Clean the surface of the ferrotype plate thoroughly with warm water or alcohol, and then cover it with a very thin layer of wax applied to the surface in the form of a solution of beeswax in benzene or use one of the solutions prepared for the purpose, such as the Ingento Polishing Compound. Let the plate stand for a few minutes until the solvent has evaporated, leaving the waxed surface, and then rub vigorously until the excess wax has been removed and a brilliant polish results. Five or six drops of the polishing solution is enough for the purpose.

If many photographs are to be preserved, some sort of a card on which the prints can be mounted for filing is useful. Figure 50 shows a style of mount suitable for general purposes.

CHAPTER XXIV

THE METALLOGRAPHIC CONSTITUENTS OF IRON AND STEEL

Although it is not necessary to consider in detail the many changes which may take place when melted alloys solidify, the changes which occur during the heating and cooling of iron-carbon alloys (iron and steel) have such an important bearing on their physical properties, that the equilibrium diagram of these alloys will be considered briefly, as it indicates graphically the condition in which the alloys exist at different temperatures and with varying carbon content. In order to make the fairly complex iron-carbon diagram more clearly understood, it is perhaps worth while to discuss some of the simpler types of alloy diagrams, of which the steel diagram is a composite.

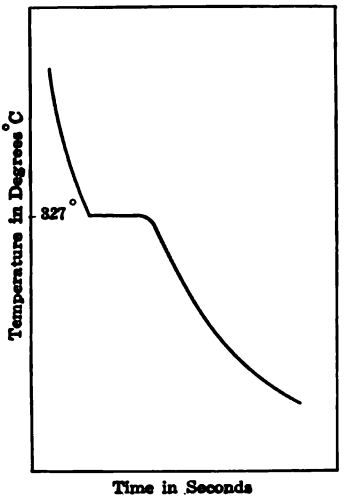


FIG. 51.—Cooling curve of pure lead.

The Eutectic Alloy.—When a pure metal solidifies from the melted condition and the temperature changes which take place during the cooling are indicated in a graphical form, a curve, in which temperatures are represented as ordinates and time intervals between temperature readings as abscissas, may be constructed (Fig. 51). The solidification of lead has been selected as an example, with intervals of 10 sec. between each temperature reading. It will be noticed that the curve falls smoothly until the temperature of 327°C. is reached, when it breaks sharply and remains horizontal, indicating a constant temperature during an appreciable period. The curve again falls gradually to room

temperature without further abrupt changes in direction. The horizontal line represents the transition of the lead from the liquid to the solid state. It is a well-known fact that in most cases in which one substance is added to another, in which it will dissolve, the freezing point of the solvent is lowered perceptibly. A common illustration of this phenomenon is the preparation of the ice-salt freezing mixture which can produce a temperature $-21°$ C. Numerous alloys behave in the same way; one of the best known of which is that of lead with antimony. If a small amount of lead is added to molten antimony, the freezing point of the latter is lowered and increasing quantities of lead

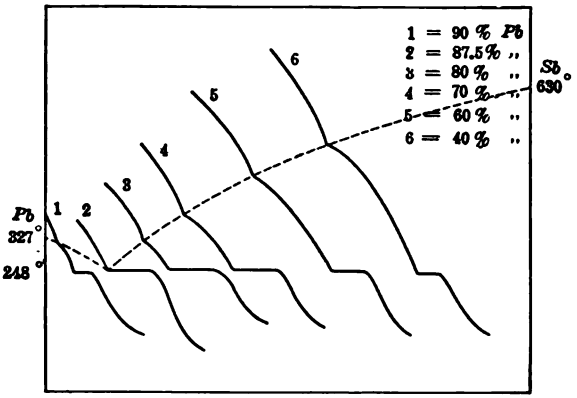


FIG. 52.—Lead-antimony cooling curves.

still further lower the freezing point. If, on the other hand, antimony is added to pure lead the melting point of the lead is lowered and, as in the case of antimony, is progressively lowered by the addition of greater quantities of antimony. The effect of the addition of each metal to the other is shown in the series of curves of Fig. 52. It is obvious that since each metal lowers the freezing point of the other, the lines connecting these freezing points must intersect at some point as shown by the dotted lines in the drawing, Fig. 52. This point is called the **eutectic point,** the alloy corresponding to the intersection of the two lines the **eutectic alloy** and the temperature at which the lines cross, the **eutectic temperature.** If the data given by the cooling curves of Fig. 52 is assembled in the form of an equilibrium diagram, the

diagram takes the form indicated in Fig. 53 in which the ordinates are temperatures and the abscissas, percentage compositions of the series of alloys studied. The lines *PbB* and *SbB* together form the freezing point diagram, as the freezing points of all lead-antimony alloys lie on this V-shaped curve. The line *DBE* indicates the temperature at which the second heat effect occurs in all alloys of this series and corresponds to the horizontal lines in Fig. 52. *DBE* is called the eutectic line. The meaning of a diagram of this type can be understood more readily by considering the physical changes which take place in a few special cases as, for example, during the cooling of alloys 1, 2, 3, in Fig. 53. Since

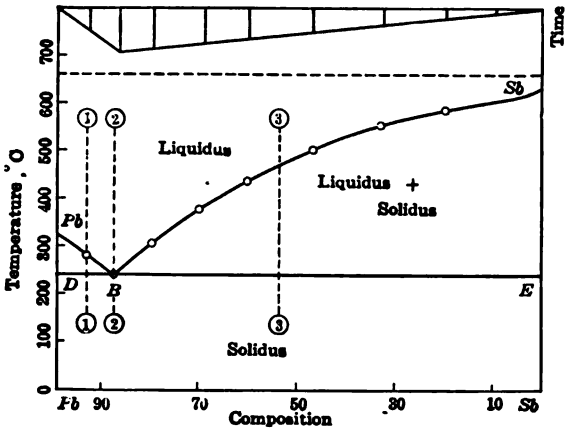


FIG. 53.—Lead-antimony diagram.

the *V*-shaped curve was obtained by connecting the freezing points of the separate alloys, it is evident that the area above the *V* represents a temperature range in which everything is in the molten condition. As the temperature of alloy 1 falls, no change takes place until the line *PbB* is reached, when pure lead begins to separate. The result of the separation is to leave a solution richer in antimony than the original and, therefore, one which has a lower freezing point. Pure lead continues to separate with the consequent formation of solutions increasingly richer in antimony and therefore with lower freezing points. As the liquid from which the lead is separating becomes richer in antimony it approaches the eutectic composition indicated by *B*. Since this

represents the lowest possible temperature at which any lead and antimony alloy can solidify, it is evident that when the residual liquid finally reaches the eutectic composition, the remaining metal will solidify at this constant temperature. The same reasoning applies to alloy 3 except that in this case the antimony crystals separate first. The primary separation of antimony is followed by an enrichment of the remaining liquid with lead until the eutectic composition is reached again. At the composition represented by alloy 2 no change takes place until the eutectic temperature is reached when lead and antimony separate together in the form of the eutectic mixture. If equal weights of the mixture of the two metals were taken for each alloy indicated on the diagram, the number of seconds taken for the liquid of eutectic composition to solidify would depend on the amount of material of this composition present in each case. This would be greatest at the composition *B*, where only eutectic is found, and would decrease right and left from this point, as the excess of antimony or lead over the eutectic composition increased. The shortening of the time for the solidification of the alloy of eutectic composition is indicated in the triangular area marked "Time" in the upper part of Fig. 53.

FIG. 54.—Bismuth-tin eutectic containing a slight excess of tin. (*Sawyer.*)

Because of the constant temperature at which the eutectic separates, it was formerly believed that the eutectic was a compound. The microscope shows clearly that this is not the case, but that, on the contrary, the eutectic alloy is an extremely intimate mixture of the two component metals. (See Fig. 54, the eutectic of bismuth-tin with a slight excess of tin.) Since the eutectic is a mixture of the two metals and since, as shown in the

diagram, Fig. 53, the eutectic line extends from one side of the diagram to the other, it follows that while lead and antimony are wholly miscible and soluble in each other in the liquid state, they are wholly non-miscible or insoluble in each other in the solid state. That the metals are insoluble in each other in the solid state must be true for the diagram shows that no matter how small an amount of either metal is added to the other, there is always the secondary heat effect at the eutectic temperature.[1]

The Solid Solution.—A second relationship which may exist between metals and one of the greatest importance in connection with steel, is a partial or complete solubility of one metal or element in another, in the solid state as well as when the metals are molten. This relation is known as the formation of a solid solution. The solid solution differs from the liquid solution simply in its physical condition. Like the liquid solution, it is perfectly homogeneous and may be saturated or unsaturated. Metal A may retain 10 per cent of metal B in the solid state, but if an attempt is made to add 12 per cent of B, the solid solution which separates on cooling is a saturated solution of 10 per cent B in A. The excess B remains in the liquid to separate later as a part of a eutectic mixture, as a constituent of an intermetallic compound or in some other form. This conception of the solid solution as wholly analagous to the liquid solution makes the graphical representation easier to understand.

Consider as an example the diagram of the alloys of copper and silver, Fig. 55. This differs from the simple eutectic diagram shown in Fig. 53 only in the location on it of the lines Ag-α and Cu-β, the significance of which is merely that molten silver, in which copper has been dissolved, is able to retain about 6 per cent of copper after the silver has solidified and that molten copper in its turn, is capable of retaining an equal amount of silver in the solid state. When an alloy of silver and copper containing less than 29 per cent of copper is allowed to solidify, the crystal which first separates is not the pure element, as in the case of the separation of lead in the cooling of the lead antimony alloys, but is a homogeneous, crystalline solution of copper in silver. The meaning

[1] It is probably not true that any two metals are absolutely insoluble in each other in the solid state but the solubility in many cases is so slight that it cannot be detected by the usual temperature measurements.

of the diagram, then, is as follows: Any alloy of silver and copper containing less than 6 per cent of copper on the one hand, or less than 6 per cent of silver on the other, will solidify as an unsaturated solid solution which is perfectly homogeneous and under the microscope shows only the fine polyhedral lines characteristic of a single crystalline solid, Fig. 161, p. 454. If now, the amount of copper added to the silver is ever so slightly in excess of 6 per cent, the solid alloy is no longer homogeneous but shows a second structure element, in this case the eutectic *E*. It is evident, then, that in the range between the points α and β, the diagram is exactly

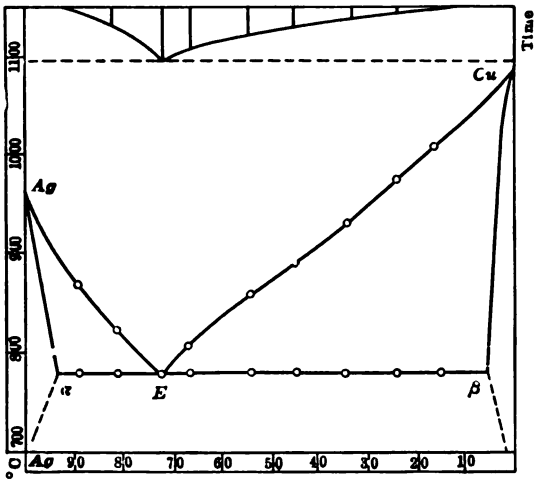


FIG. 55.—Copper-silver diagram. (*Heycock and Neville, Fredrich and Leroux.*)

analagous to the simple eutectic diagram, the only difference being that with the silver and copper alloys the constituents are not the pure metals but are the saturated solid solutions α and β.

The solubility of one metal in another may increase as shown in the series of diagrams of Fig. 56, until the condition indicated in *D* is realized. The line α-β representing the secondary or eutectic separation, has gradually shortened, with the increase in the mutual solubility of the two metals, until in the alloy *D* the line has disappeared wholly, showing that the metals are soluble in each other in all proportions in the solid state. Diagrams *A* and *D* differ radically in this respect, although both show

the two metals to be soluble in each other in all proportions in the liquid state and, also, that each metal lowers the melting point of the other, diagram *A* indicates that the two metals are completely insoluble in each other in the solid state while diagram *D* shows that the two solid metals are soluble in each other. Alloy *E* in diagram *A* is as inhomogeneous as possible while $\alpha\beta$ in diagram *D* is perfectly homogeneous and represents simply that

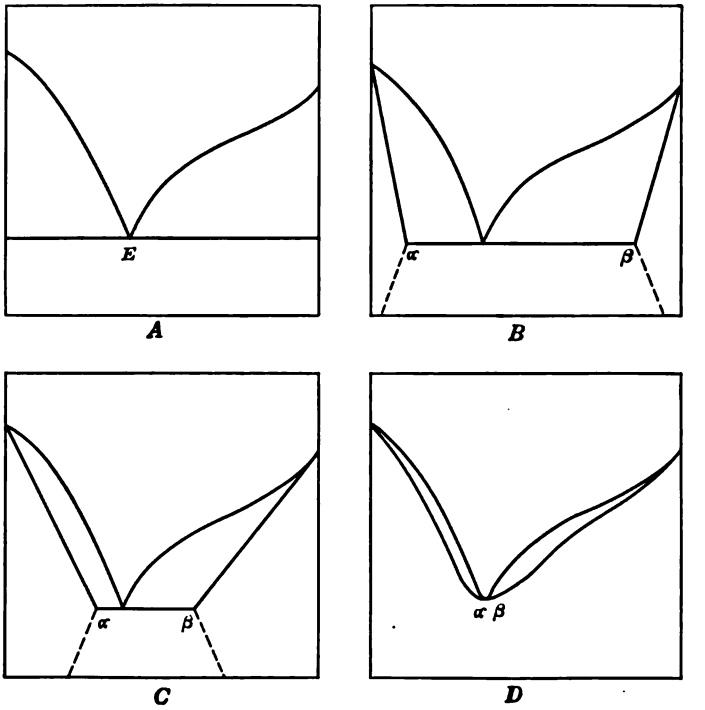


FIG. 56.—Development of the solid solution.

one of a series of perfect solutions which has a melting point lower than that of any of the other solid solutions in the series. This is often referred to as the solid solution minimum. A second type of solid solution includes that class of alloys in which the metals are mutually soluble in all proportions but whose diagram shows no minimum. A relation of this sort is shown in the diagram of the copper-nickel alloys, Fig. 57. In

addition to the types of alloys indicated in Figs. 53, 55 and 57, various other reactions may take place in the cooling of a mixture of metals from the molten state as, for example, the formation of one or more intermetallic compounds or a partial separation into liquid layers. A discussion of these other types belongs to the field of general metallography and has no immediate connection with the present problem.

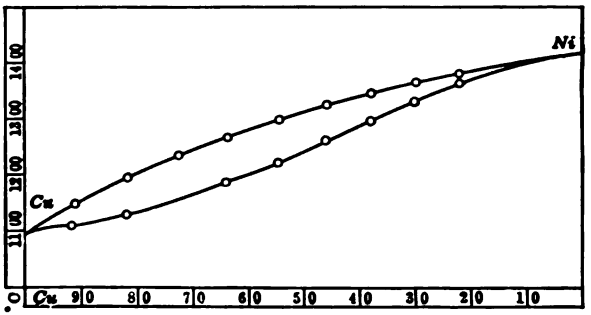


FIG. 57.—Copper-nickel alloys. (*Guertler and Tamman.*)

Changes in the Solid Alloy.—The diagrams which have been considered, have dealt with changes which occur when the alloy passes from the liquid to the solid state or *vice versa*. Some of the most valuable technical alloys, notably steel, acquire their properties or modify them materially because of changes which take place in the solid state. Iron, for example is believed to exist in at least three allotropic forms α-iron stable below 780°C., β-iron existing between 780 and 900°C. and finally γ-iron stable above 900°C. and practically non-magnetic. While these magnetic changes are of interest to the physicist, the fact of importance to the metallographer is that γ-iron will hold carbon in solid solution but α- and β-iron will not. This means then, that when the iron-carbon alloy is cooled, a change in components, and therefore in physical properties, occurs in passing from the γ-iron range to the α-iron range even though the alloy in the γ-field is perfectly solid.

More important than the changes due to the allotropism of a single metal are those changes which come from the decomposition of a solid solution at temperatures below its freezing point. All the changes which can take place when a liquid solution

freezes may also occur when a solid solution decomposed. It may change to a eutectic-like mixture, to another solid solution more or less complete or it may decompose to form one or more compounds. Some of these possible changes are indicated in Fig. 58. The most important of these transformations in the solid state is that shown in I of the figure, as many of the valuable properties of steel, given to it by heat treatment, are due to decompositions of this sort. Transformation of a solid alloy of the solid solution type to one of a different character, requires a definite amount of time, and by shortening this time, the transformation can be partially or wholly suspended. For example, by suddenly cooling (quenching) an alloy from the temperature indicated by x in Fig. 58, I, it is possible to prevent the trans-

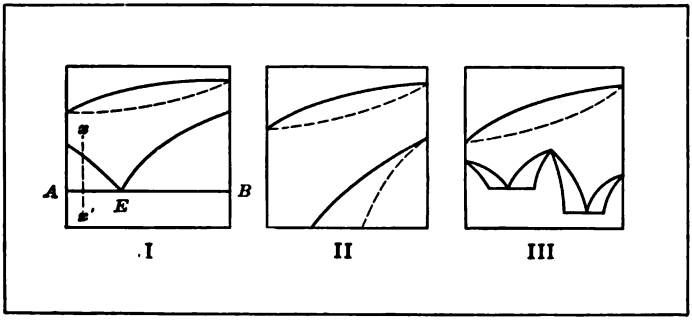


FIG. 58.—Types of changes occurring in the solid state.

formation, of the solid alloy along AE, into that represented by x', with the result that at ordinary temperatures the alloy exists in the condition which it had at the higher temperature x. The physical properties of a solid solution are so different from those of the eutectic-like mixture that by more or less completely checking the change from x to x' the mechanical properties of the alloy can be profoundly modified and can be controlled within fairly definite limits. The alloy represented by the point E, Fig. 58, I, has all the characteristics of the eutectic including the "thumb print" structure as seen under the microscope. Since, however, the separation of the constituents takes place from a solid solution, instead of from a liquid, the name **eutectoid** is commonly given to it.

Bearing in mind the significance of the several types of alloy diagrams just considered, the interpretation of the iron-carbon diagram, Fig. 59, is not difficult as it will be seen to contain (1)

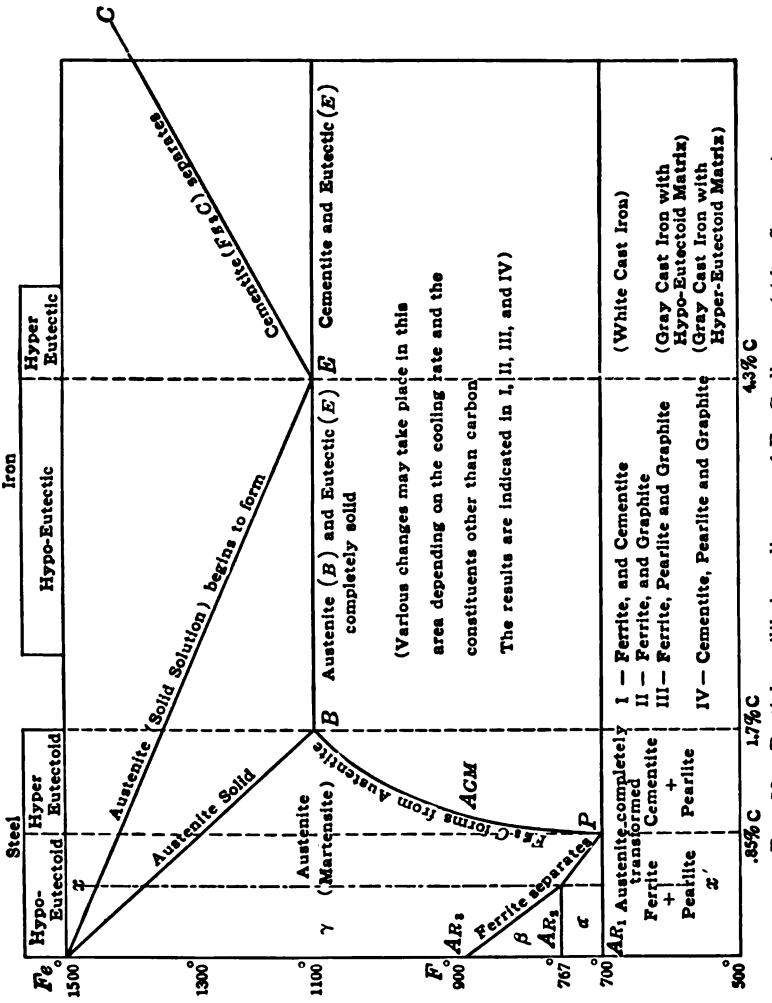


FIG. 59.—Partial equilibrium diagram of Fe-C alloys. (*After Sauveur.*)

solid solutions in the area *FeFPB*, (2) the eutectoid *P*, and (3) the eutectic *E*, the two components of which are the saturated solid solution *B* and the substance which separates along the line

CE, which in this case is not pure carbon but a compound which has been shown by chemical analysis to have the symbol Fe_3C. The same compound separates along the line *BP* and is one of the two components of the eutectoid *P*, of which pure iron is the other constituent. The diagram indicates that iron will dissolve carbon with the formation of a solid solution, which becomes saturated when the carbon content has reached approximately 1.7 per cent. The area *FeFPB* includes the steels, while the cast and pig iron range includes the iron-carbon alloys varying in composition from 1.7 per cent carbon up to 5 or 6 per cent. The single exception to this classification is the **wrought iron** (p. 367) whose carbon content is commonly less than 0.3 per cent. In the steel section of the diagram, the solid solution included in the area *FeFPB* decomposes along the lines *FP* and *PB* into various mixtures of pure iron (ferrite) and the eutectoid *P*, when the carbon content is less than 0.85 per cent, or into iron carbide (Fe_3C) and the same eutectoid, when the percentage of carbon is greater than that shown by the point *P*. If such decomposition always took place, regardless of the cooling rate, there would be only three classes of steel, (1) pure iron with varying amounts of the eutectoid *P*, (2) the eutectoid itself and (3) ferric carbide with varying amounts of the eutectoid, and the study of steel would be a comparatively simple matter. The valuable properties of steel and the fact that its properties can be profoundly changed by heat treatment are due to the slow decomposition of the solid solution into its final components. This gives to the steel maker the power of controlling the amount of decomposition to a marked degree, by means of cooling and heating operations, such as quenching, tempering and annealing. If the solid solution could be kept wholly unchanged by sufficiently rapid cooling (quenching), the component to which the name **Austenite** has been given would be found. This can hardly be done with plain carbon steel, though austenite is a common constituent of steels containing manganese, nickel and other metals. In practice, quenching commonly produces the first stage in the decomposition of austenite on its way to the eutectoid, and the resulting material has been called **Martensite.** Still slower cooling or, more commonly in practice, reheating, leads to the formation of **Troostite,** which in its turn is followed

by **Sorbite** and finally, very slow cooling of the steel produces the last stage in the decomposition of the solid solution, namely the eutectoid **Pearlite.** The transition briefly stated is Austenite →Martensite→Troostite→Sorbite→Pearlite. Pure iron which separates along the line FP is called **Ferrite,** and iron carbide is known as **Cementite.** A brief description of these constituents with the methods of their formation will be given shortly. The constituents of cast iron vary considerably with the method of production of the iron and with the constituents other than carbon which may be present. The components not usually found in steel are **Graphite** and **Graphitic temper** carbon and the eutectic E, known as **Ledeburite,** though this component is not often named.

Etching of Steel and Iron.—Many more or less complex solutions have been tried for the etching of steel, but for the purposes of the control laboratory a few of the simpler ones will serve every purpose.

Nitric Acid and Alcohol.—The most useful of all etching reagents for steel is a solution containing 4 c.c. of concentrated nitric acid (d. 1.42) in 96 c.c. of ethyl alcohol. The specimen is immersed face up in the solution and is kept in constant motion to prevent the formation of gas bubbles on the polished surface. The time required for etching varies from 2 to 3 sec. with troostite, requires about 5 sec. for martensite and from 7 to 10 sec. for sorbite and pearlite. After the specimen is etched, it is dried with a soft cloth or with a warm blast of air.

Picric Acid.—A solution of 5 g. of picric acid in 95 c.c. of ethyl alcohol is often used for low-carbon steels.

Alcoholic Hydrochloric Acid recommended by Martens and Heyn, is made by dissolving 1 c.c. of concentrated hydrochloric acid (d. 1.19) in 100 c.c. of alcohol. This reagent requires that the sample be immersed from six to eight times as long as with nitric acid but gives excellent results.

Kourbatoff's Reagent for Cementite.—Cementite is not attacked by the usual etching reagents, but is colored black or brown by immersion for a period of 3 to 5 min. in a boiling solution of sodium picrate in sodium hydroxide. The reagent is made by dissolving 2 g. of sodium picrate in 98 c.c. of a 25 per cent solution of sodium hydroxide. Ferrite is not affected by this reagent so

that it is possible to distinguish positively between the two constituents, cementite and ferrite.

To refer again to the diagram p. 356, austenite is the solid solution of carbon or iron carbide in γ-iron, and is the component that would be expected when a steel is quenched as quickly as possible from a high temperature. The transition to martensite takes place so easily, however, that austenite is seldom formed in the commercial hardening of plain carbon steels. It may be obtained readily by quenching a steel containing manganese in fairly large quantities (10 per cent for example). Austenite is almost always accompanied by martensite. A characteristic photograph of the combination is shown in Fig. 60. The unetched surface is austenite, and the dark zigzag needles are martensite.

FIG. 60.—Austenite and martensite.

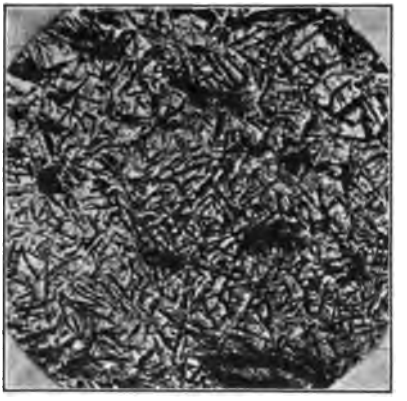


FIG. 61.—Martensite. 100 ×. (*Homerberg.*)

Martensite. — This component represents the first stage in the decomposition of the solid solution. Pure martensite is obtained by quenching small pieces of steel at a high temperature, and is characterized by its needle-like structure which becomes more strongly marked the longer the etching is continued. Some of the needles are more strongly attacked than others, and as a result a marked roughening of the surface is

produced. As shown in Fig. 61, the needles intersect at about 60°C. producing the triangular appearance which is characteristic of the martensitic structure. If the cooling of the solid solution takes place somewhat less rapidly, the second step in the decomposition occurs, and the martensite is found associated with the constituent troostite.

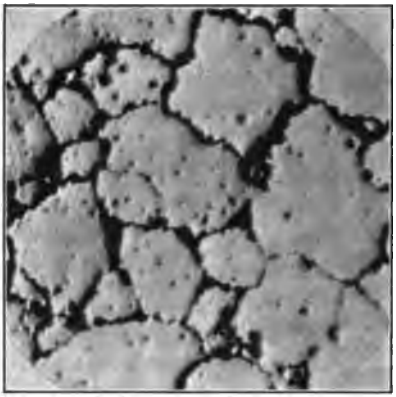


FIG. 62.—Martensite and troostite. 100 ×. (*Homerberg.*)

Troostite.—In order to indicate the relation between martensite and troostite, the latter may be considered as the product of a cooling which is somewhat slower than that needed to produce martensite. In commercial practice, however, troostite is almost always formed by reheating (tempering) quenched steel at a temperature lower than 400°C. The characteristic properties of troostite are the rapidity with which it is colored by etching reagents and the dark color produced. Under the microscope it is found, usually associated with martensite, in the form of black irregular patches or nodules often occurring at the boundaries of the martensite grains. The nearer the temperature of reheating approaches 400°C., the greater will be the relative amount of troostite and the softer the material, as compared to that of martensite, so that by regulating the temperature the amount of troostite, and therefore the hardness and toughness of the steel, can be altered within fairly wide limits. Figures 62 and 63 illustrate the general appearance of troostitic steel.

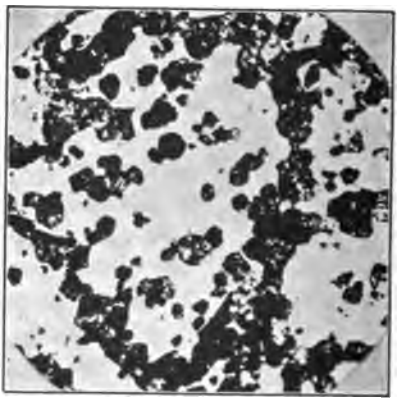


FIG. 63.—Troostite and martensite. 100 ×. (*Homerberg.*)

Sorbite.—One more step in the transition of the solid solution from austenite to pearlite leads to the formation of the material, sorbite, which may be considered either as partially decomposed troostite or as imperfectly formed pearlite. Its relation to troostite may be shown by heating a specimen containing troostite to a temperature between 400 and 600°C., and, on the other hand, its nearness to pearlite may be shown by cooling the heated steel at such a rate that pearlite just fails to be formed. The microscopic appearance of sorbite varies with its method of formation, but in general it resembles the structure shown in Fig. 64.

FIG. 64.—Sorbite. 100 ×. (*Fay.*)

Pearlite.—The last stage in the decomposition of the solid solution leads to the formation of the eutectoid P, Fig. 59, which because of its resemblance under certain conditions to mother of pearl, has been called pearlite. It consists of alternate layers of ferrite (pure iron) and cementite which, after treatment with the etching reagent, give to the specimen a characteristic thumb print structure. The microscopic appearance of pearlite varies considerably with the manner of its formation. If the steel is cooled rapidly through the critical range, it may have the poorly-defined structure of sorbitic pearlite but, with decreasing cooling rate, the clearly-marked, laminated structure becomes increasingly evident, Fig. 65. An abnormal case of decomposed pearlite is illustrated in Fig. 66, an

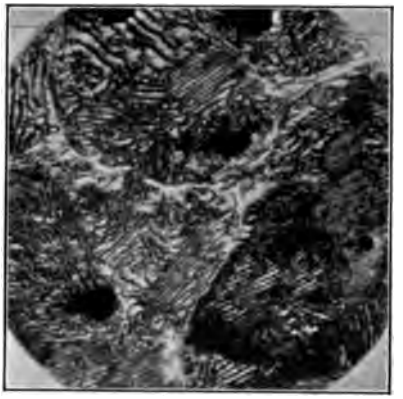


FIG. 65.—Pearlite and temper carbon. (*Fay.*)

example of what is commonly known as **spheroidized cementite.** When the pearlite is heated for a long time at 600 to 700°C.,

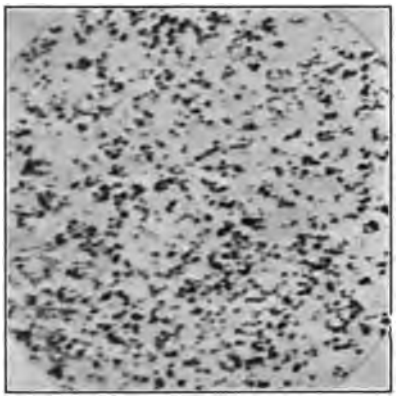
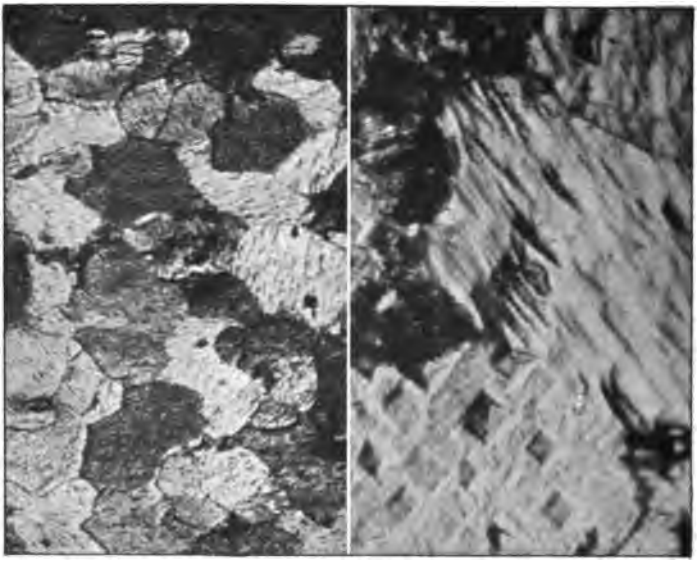


FIG. 66.—Spheroidized cementite. 100 ×. (*Homerberg.*)



365 × 1650 ×

FIG. 67.—Ferrite.

the cementite which the pearlite contains, coagulates into spherical masses, giving a steel which is weaker and softer than the

corresponding pearlite, but is more ductile and has greater wearing qualities.

Along the line FP Fig. 59 a separation of pure iron, to which the name **ferrite** has been given, takes place. Pure ferrite, seen without the microscope, has the appearance of a rough surface, which the microscope shows to be due to the presence of "etch-figures." The right-half of Fig. 67 shows the symmetrical arrangement of the etch-figures on the ferrite grains, produced in this case by etching with copper ammonium chloride (p. 373). Associated with pearlite, ferrite is the white structureless constituent.

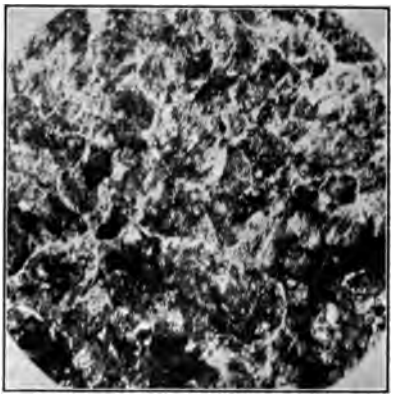


FIG. 68. — Pearlite and cementite. Etched with alcoholic nitric acid. 100 ×. (*Homerberg.*)

The last of the microscopic constituents commonly considered is the chemical compound **cementite.** This substance separates along the line BP, and is white and practically unaffected by ordinary etching reagents. It is distinguished from ferrite by the fact that it is colored brown or black by alkaline sodium picrate (p. 358). Figures 68 and 69 show the appearance of cementite and pearlite, the first etched with alcoholic nitric acid and the second with Kourbatoff's reagent.

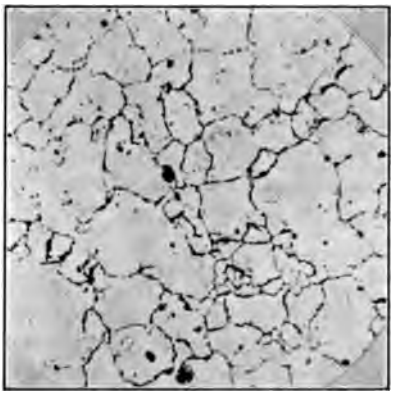


FIG. 69. — Pearlite and cementite. Etched with Kourbatoff's reagent. 100 ×. (*Homerberg.*)

The name **osmondite** is sometimes given to that constituent which is formed by tempering martensite at exactly 400°C. It lies at the boundary between sorbite and troostite, and differs somewhat from each

in its appearance. The name is seldom used by American metallographers.

In the iron range (above 1.7 per cent C.), the metallographic constituents which are characteristic are the two forms of graphite and the eutectic. Primary **graphite** occurs in the form of clusters of needles or in long plates or veins. The halves of Fig. 70 show the two types of graphite crystals as they occur in different sorts of cast iron. Etching is not necessary to develop the structure of iron containing crystalline graphite.

FIG. 70.—Graphite in iron. 117 ×.

The second form of carbon is that illustrated in Figs. 71 and 72 showing the **graphitic temper carbon,** which is produced in the manufacture of malleable castings. Chemically, it is composed of pure carbon just as crystalline graphite is, but physically it is quite different in its properties and appearance. It occurs most commonly in the form of irregular black spots nearly circular in form.

The eutectic has the thumb print structure shown in Fig. 73 and is sometimes called **ledeburite.**

In addition to the normal constituents described above, there are many abnormal components like slag, sulphides of iron

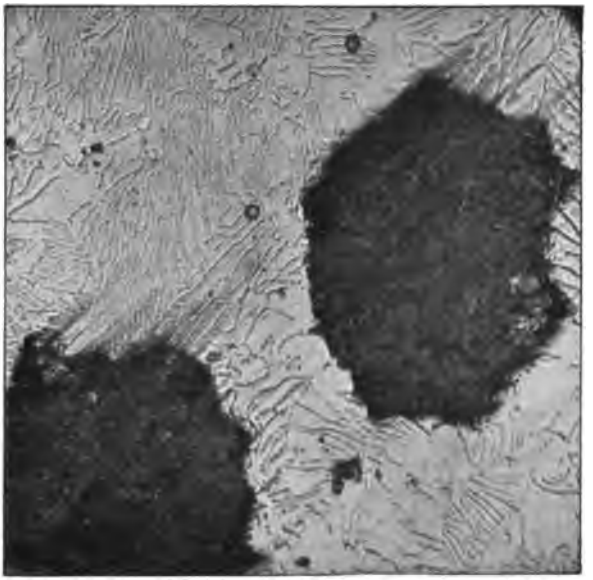


FIG. 71.—Temper carbon in iron. 350 ×.

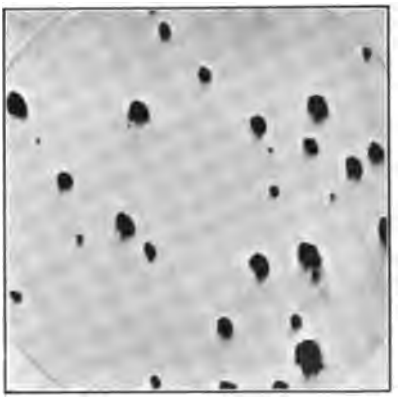


FIG. 72.—Temper carbon in iron.

or manganese and the like. These components are considered in connection with the particular classes of iron or steel in which

they most commonly occur. In the chapters which follow, the various classes of iron and steel are discussed with special reference to the applications of the microscope, both as an aid to sampling for chemical analysis and as an additional means of determining the nature of a given specimen and its suitability

FIG. 73.—Ledeburite and martensite. 350 ×.

for the intended purpose. It will be impossible, of course, to illustrate many cases of good and bad material, but it is hoped that, from the examples given, enough suggestions will be found to make the microscope of real use to the analyst and metal tester.

CHAPTER XXV

WROUGHT IRON AND STEEL

Wrought iron is made by melting pig iron, as it comes from the smelting furnace, with iron oxide. The resulting pasty mass is then hammered and rolled to remove most of the impurities. The carbon content is low, usually less than 0.3 per cent,

FIG. 74. Wrought iron made by busheling scrap iron.

so that the resulting iron consists chiefly of ferrite with such impurities (mostly an iron silicate slag), as have not been removed from it by the rolling operation. Instead of making wrought iron from pig iron and oxide, it is sometimes produced by heating scrap iron to a semi-pasty mass and then rolling it together. Such a method of manufacture leads to very great irregularities due to the differences in the scrap iron, and its character can be

determined by microscopic examination far more readily than in any other way, Fig. 74. Wrought iron, as commonly prepared, is distinguished by the slag spots and streaks, which

FIG. 75.—Slag in wrought iron. Longitudinal section. 100 ×. (*Homerberg.*)

it contains, and which make it difficult to obtain a representative sample. Figures 75 and 76 show the usual appearance of wrought iron, Fig. 75 showing the appearance of a section made in the

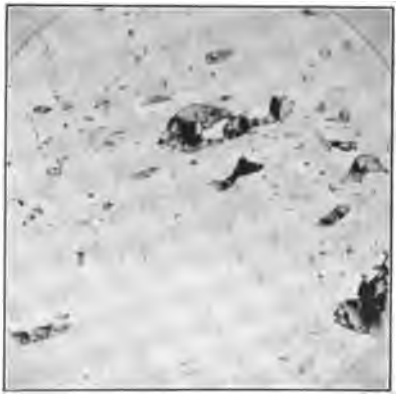


FIG. 76.—Slag in wrought iron. Transverse section. 100 ×. (*Homerberg.*)

direction of rolling and Fig. 76, the same specimen photographed at right angles to the direction of work. While the slag in this specimen is fairly uniformly distributed, it happens not infre-

quently that the distribution is very uneven as is shown in Fig. 77. If the analyst wishes to determine the composition of the slag, he can most readily find its location by the microscope, while if he wants an average sample, he will make his sampling much more representative through metallographic examination which will show him the distribution of the impurities. The following table illustrates the marked differences that may be found in the analysis if the sampling is not carried out with unusual care.

FIG. 77.—Slag inclusions in wrought iron. 350 ×.

TABLE IV

Samples taken	Phosphorus, per cent
By planing over the cross-section	0.17
By boring in the dark spots	0.30

Cast steel has been a difficult material with which to work successfully in the past, but with improved methods of melting and temperature control its use is constantly increasing, especially in the production of small castings. The microscopic appearance of cast steel is such as would be predicted from the diagram p. 356. In the low-carbon ranges, the surface shows a mixture

of ferrite and pearlite; at the eutectoid composition, only pearlite is visible and, in the high-carbon cast steels (almost never found in practice), cementite and pearlite are seen. The microscope can be of great service in the examination and control of cast steel for several reasons. In the first place, the castings are likely to contain blow holes or slag (oxide) spots unless they are skilfully melted and poured. Both of these imperfections are easily found on the polished specimen. The most serious imperfection in cast steel, however, results from the coarse grained structure, which is almost always found in cast material, especially in the low-carbon steels. The grain size of the cast material can be reduced by suitable annealing and this causes a marked improvement in the physical properties of the material. Figures 78 and 79 show a cast steel before and after the refinement of its grain by annealing. While the tensile strength is substantially the same before and after the anneal, the ductility is more than twice as great in the steel shown in Fig. 79 as in the coarse grained, unannealed casting.

FIG. 78.—Cast steel. Unannealed. 100 ×. (*Homerberg.*)

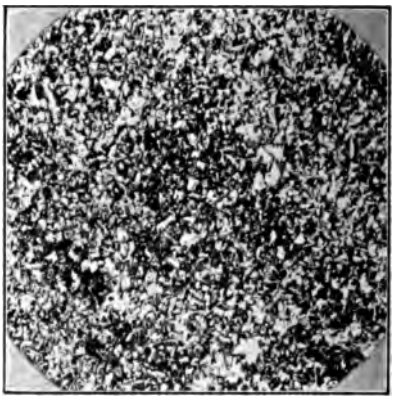


FIG. 79.—Cast steel. Annealed. 100 ×. (*Homerberg.*)

Steel.—The term steel covers so vast a range of possible conditions in the alloys of iron and carbon that anything like a complete discussion of the many varieties is a study in itself.[1] It will be possible here to con-

[1] See SAUVEUR, "Metallography and Heat Treatment of Iron and Steel."

sider only those features of the subject which deal especially with questions of sampling and with abnormalities like phosphorus segregations, sulphide inclusions and the like, which are of special interest to the analyst and inspector of metals.

Chemical and Metallographic Study of the Solid Ingot.—If samples are not taken during the pouring as described later (p. 427) not only is it difficult, expensive and time-consuming to get shavings from the ingot which really represent the composition of the original charge, but in the case of large ingots it is absolutely impossible.

Molten iron forms a solid solution with most of the foreign elements occurring with it. As regards the solidification it may be said: The solid solution, as it separates, is always richer in the constituent with the highest melting point than is the melt with which the crystals are in equilibrium; or, in other words, the melt retains more of that constituent by means of which the solidification temperature was lowered than is present in the crystals first formed.

Now since the temperature at which pure iron solidifies (1,505°) is lowered by all the impurities that occur in technical iron as well as by those elements which are added to it intentionally, it follows that when a large ingot solidifies, the solid solution that first separates on the cold walls of the mold is freer from those elements which caused the lower melting point (chiefly carbon, phosphorus, sulphur and manganese) than that part of the melt which cools more slowly. These foreign elements, therefore, are forced continuously toward that part of the casting which solidifies last. In the case of large ingots this point lies in the middle of the ingot near its head as indicated in Fig. 80. Segregation, therefore, takes place during the cooling.

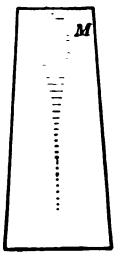


FIG. 80.

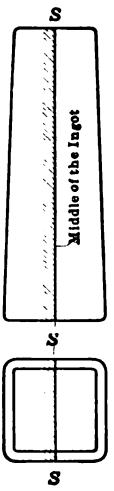


FIG. 81.

To determine by chemical means the extent to which segregation has taken place, an ingot may be cut lengthwise along the line *S*-*S* (Fig. 81) and borings taken at various points of the surface indicated in the drawing by cross-hatching. If the results

of the analyses of samples taken from various places on the section are plotted (see Fig. 82) it is possible to get a fairly good idea of the distribution of the various constituents in the ingot. It must be remembered in this connection that these analyses give only the composition of a few selected points and that their average does not by any means represent the average composition of the ingot.

As a rule segregation takes place to a greater extent as the quantity of elements other than iron in the charge is increased.

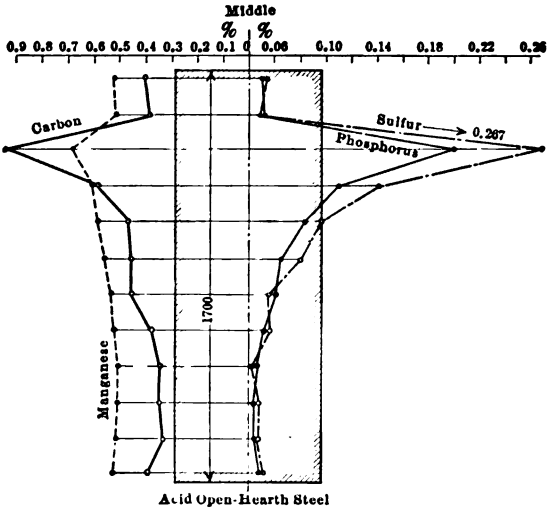


FIG. 82.

This is shown clearly in the following example.[1] The average composition of an acid open-hearth steel (samples taken from the ladle) was 0.38 per cent carbon, 0.052 per cent phosphorus, 0.52 per cent manganese and 0.061 per cent sulfur. The ingot showed marked segregation as illustrated in Fig. 82. (The analyses selected were from a section taken through the middle of the ingot.) The top of the ingot was particularly rich in phosphorus and sulfur and there was also a decided segregation of carbon.

The question as to whether segregation exists or not is of the

[1] TALBOT, *Iron and Steel Institute*, 1905.

greatest practical importance, because the usefulness of the material for a definite purpose is often determined by the presence or absence of marked segregation.

The nearer together the points from which the borings are taken, the more definite is the knowledge of the way in which the foreign elements are distributed. A purely chemical study like the one just described is very time-consuming and expensive and, moreover, the ingot must be remelted as it is no longer suitable for rolling.

Macroscopic Examination of Steel.—Under conditions of this kind, the *macroscopic* examination of the specimen has been very successful in detecting segregation in the material, particularly the segregation of phosphorus and sulfur. Studies of metallic surfaces with magnifications of less than ten diameters are classed as macroscopic, and the corresponding photographs (most commonly not magnified at all) are called macrographs.

The preparation of the surface for macroscopic examination requires somewhat less care than is needed for the preparation of a micro-specimen. The following procedure will be found satisfactory in most cases: First, plane or file the surface until it is smooth. Remove the marks of the plane or file with emery paper using one or two grades if needed, and finally finish with fine emery powder or rouge on a rotating disk. With small specimens, the sample can be held against the rotating wheel, but with large pieces, the disk should be so arranged that it can be moved to any position on the surface to be polished. The more perfectly the specimen is polished, the better defined will be the macroscopic structure, but for many purposes polishing with fine emery paper will be enough, without the use of the finer abrasives.

Etching Reagents for Macroscopic Examination.—Three types of reagents are used for this work: (1) Quick acting solvents, (2) slow solvents, (3) reagents for a special constituent.

In the first class are concentrated hydrochloric acid, which is not often used; the iodide reagent, which is made by dissolving 10 parts of iodine in a solution of 20 parts of potassium iodide in 100 parts of water, and finally Heyn's reagent. The last is the most useful of the three and is made by dissolving 10 parts of the double chloride of copper and ammonium in 120 parts of

water. The solution is allowed to stand for a time after which the precipitate is separated from the solution by decantation. A solution prepared in this way will keep indefinitely.

The second class is composed of the dilute acids. Sulfuric acid containing 20 c.c. of concentrated acid in 100 c.c. of water may be taken as a type. Etching in this case is a slow process, requiring from a few hours to several days, but the results are excellent.

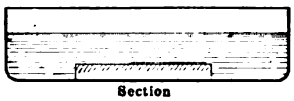


FIG. 83.—Etching dish with section.

The third class of special reagents includes those which are used to detect sulphide and phosphide inclusions, and their method of application differs so much from that usually adopted that they are considered in a separate section (*cf.* p. 378).

Reagents of the two first classes are best used by immersion of the polished specimen as indicated in Figs. 83 and 84. If this is not practicable, because of the size of the specimen or for lack of a suitable container for the reagent, the specimen may be etched by swabbing with cotton wool soaked in the particular etching solution to be used. The time required to develop the structure is much longer under these conditions, and the results are not so uniform. Nevertheless, it is quite possible to get

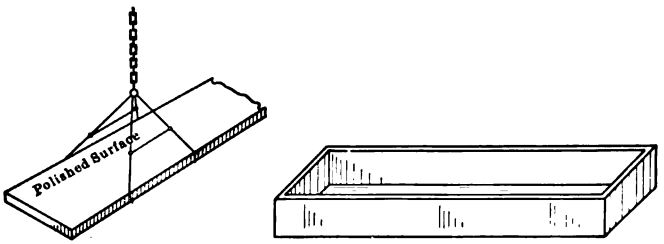


FIG. 84.—Etching of large specimen for macroscopic examination.

valuable information in this way. After etching for the required time, which is usually from 1 to 5 min., wash the specimen thoroughly with running water, rinse with alcohol and finally dry with a soft towel. Figure 85 shows a section of a 3-ton ingot polished as just described and etched with copper ammonium chloride. This ingot was prepared by the Harmet process, and will be seen to be especially free from segregation. It is

not always possible to divide a large ingot for the purposes of metallographic examination. It cannot be done, for instance, if the ingot is to be rolled or drawn. If, in such a case, it is desirable to get an approximate idea of the distribution of foreign elements in the ingot, it may be done, as indicated in Fig. 86 by taking a section at the top of the ingot, at *K*, equal to about one-fourth of the entire cross-section, a similar piece near the bottom, at *F*, where the segregation is least, and examining these specimens after polishing and etching.

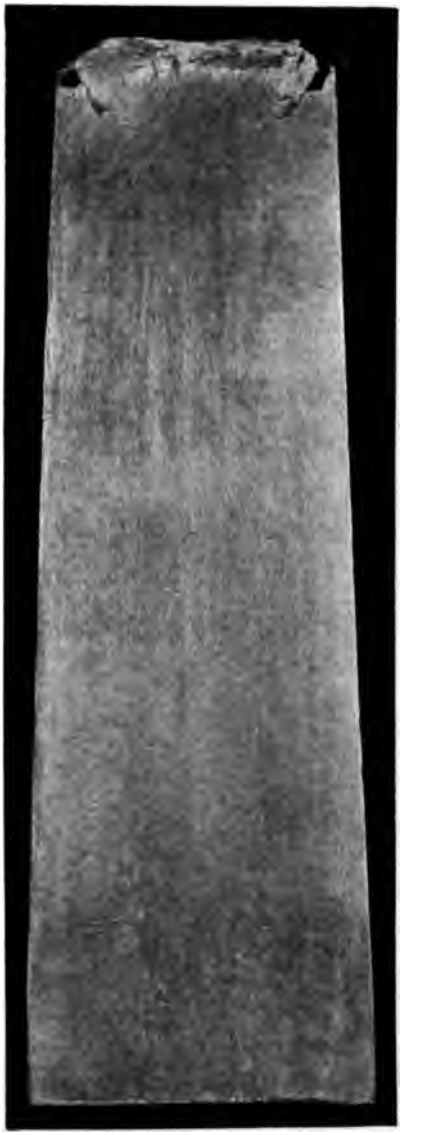


FIG. 85.—Etched section from a 3-ton ingot.

Figure 87 shows the polished section from the top of the ingot and Fig. 88 one from the bottom of an ingot of basic-Bessemer steel. The deepest black spots are due to blow holes.

A circle of large holes separates the inner from the outer zone in both sections. The core is darker in both cases than the outer edge. In this inner zone are found larger or smaller spots rich in phosphorus. A dark color after etching with copper ammonium chloride is generally an indication of a high phosphorus content. The other impurities, however, particularly the oxide and sulfide compounds, tend to

collect at those places where the phosphorus content is greatest, so that in case the color is unusually dark it is safe to assume that the sulfide and oxide content is also high.[1]

It will be noticed that at the top of the ingot the boundary between the inner and outer zones is sharply marked by a dark band, while at the lower end (Fig. 88) there is a gradual transition without any sharply marked, dividing line. The dark color in the inner zone of section, *F*, from the foot of the ingot, is very slight as compared to that of the corresponding part of the upper section, *K*. The conclusion may be drawn from these facts that there is a marked difference in the percentage of impurities at the top and at the bottom of the ingot. This opinion is confirmed by analyses made from different parts of the ingot.

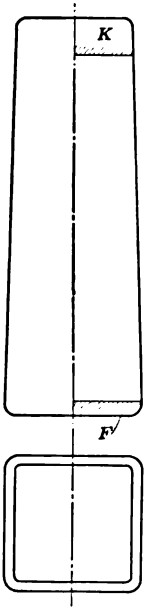


FIG. 86.

The macroscopic examination (etching test) gives, therefore, a satisfactory idea of the distribution of foreign matter in the material. It shows whether zone-formation due to segregation has occurred, the boundaries between the different zones, and gives a means of determining the most suitable places for taking samples for chemical and mechanical tests.

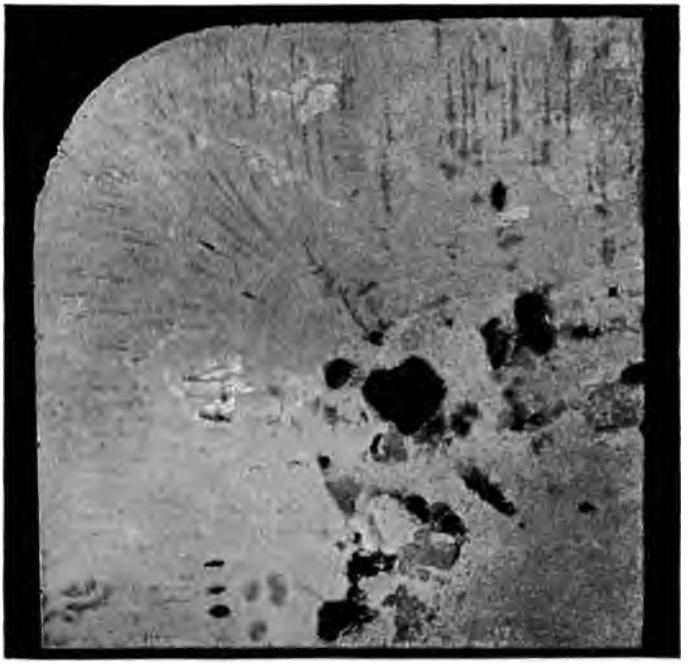
Two methods of recording the macroscopic structure of a steel without the use of the photographic plate have been devised, the first the direct sulfur print on silk or on photographic paper and the second a print made by the use

TABLE V

	From top of ingot		From bottom of ingot	
	Inside, per cent	Outside, per cent	Inside, per cent	Outside, per cent
Carbon	0.11	0.06	0.07	0.07
Manganese	0.52	0.48	0.47	0.46
Phosphorus	0.15	0.07	0.08	0.05

[1] In case of doubt, microscopic examination and the sulfur print (p. 378) will confirm or disprove the presence of these constituents.

FIG. 87.—Section *K* from the top of the ingot.



of printer's ink on the etched surface. Both of these operations come under the third class of macroscopic etching methods.

Sulfur printing depends on the fact that sulfur exists in the steel either as iron sulfide or, more commonly, manganese sulfide, both of which are readily decomposed by dilute acids with the evolution of hydrogen sulfide. In the older method of Heyn and Bauer, the polished surface was covered with a piece of white silk which was then moistened with a solution of the following composition:

10 g. mercuric chloride
20 c.c. hydrochloric acid (d. 1.12)
100 c.c. water.

Wherever sulfide inclusions are present, hydrogen sulfide is evolved, and will cause the deposition of black mercuric sulfide. The action should be allowed to continue for 4 or 5 min. The appearance of sulfur prints made in this way is shown in Figs. 89 and 90 in which the dark streaks and spots correspond to the sulfide inclusions in the sample.

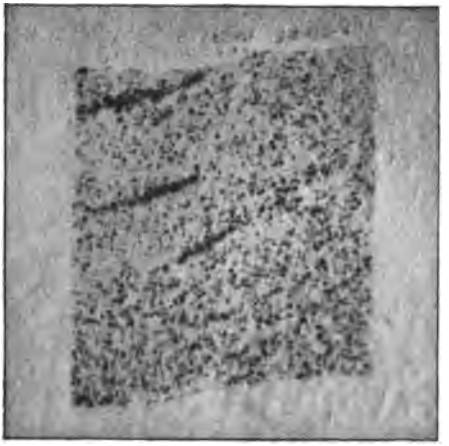


FIG. 89.—Sulfur print on silk.

Silk printing has been replaced to a considerable extent in American practice by a modification of the process suggested by Baumann. Velox, Cyko or other developing paper is soaked in dilute acid (sulfuric or hydrochloric acid having a concentration of from 2 to 10 per cent), held on the polished specimen for about 20 sec., washed in water and then fixed in "acid hypo" in the usual way. Sulfide inclusions are again indicated by black spots due, in this case, to the reaction of the evolved hydrogen sulfide with the silver of the paper.

Prints with printer's ink illustrate in a striking fashion the

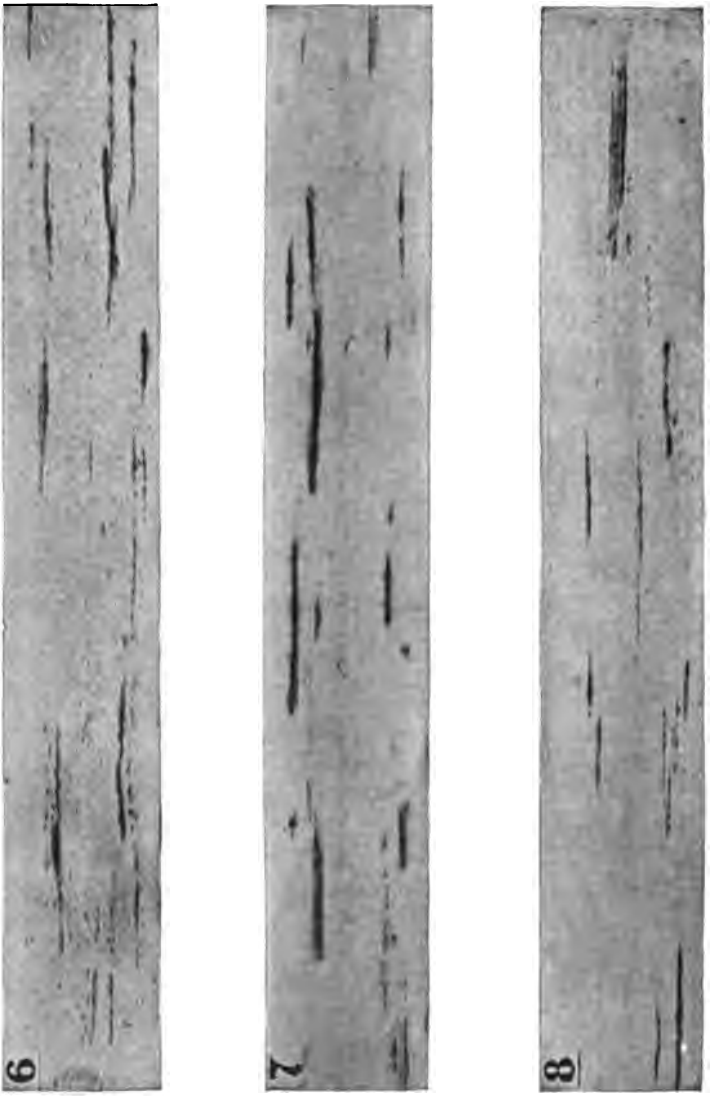


FIG. 90.—Sulfur prints of rolled plates.

larger surface features of the polished specimen. The method has been used for many years but until recently has been difficult to control. Humfrey[1] has developed an etching method which makes it possible to produce excellent direct prints from samples having the comparatively rough surface given by an emery paper finish. The reagents used are neutral copper ammonium chloride, 120 g. per liter and:

Copper ammonium chloride	120 g.
Hydrochloric acid (conc.)	50 c.c.
Water	1,000 c.c.

The exact proportion of HCl varies somewhat with different steels and must be determined by trial.

Start the etching with the neutral solution of the copper salt and continue with this reagent until the scratches left by the emery paper have been eaten away. Determine this point by wiping off the copper deposit and examining the dried surface. When the scratches have disappeared, start the etching again with enough of the neutral reagent to form a complete but thin covering of flocculent copper. Then, in successive applications, increase the acidity of the solution to its maximum. Continue the treatment with the acid reagent for about 15 min. Wipe off the deposited copper and rub the matt surface lightly to bring out the relief portions in strong contrast. The total time taken for the preparation of the specimen is from 20 min. to 1 hr.

Printing.—The most perfect reproductions of the etched surface are made by the regular book printing process, but very satisfactory results may be obtained by inking the surface of the etched specimen by means of a roller of the type used in the mimeograph, after which the impression is taken by pressing a sheet of glossy printing paper against the inked surface by means of a letter-copying press or similar device. This method has been used with great success not only in the study of ingots but also with forged or otherwise worked material.

Defective areas in the original ingot should be removed from the ingot before the steel is used for rolling, shaping or any one of

[1] J. C. W. HUMFREY, Macro-etching and macro-printing, *J. Iron and Steel Inst.*, **99** (1919) 273.

the numerous operations to which it might be subjected as it is found that imperfections in the structure of the ingot are almost invariably carried into the finished product. Here, as in the case of the ingot itself, the macroscopic examination is of the utmost value in the inspection of the material. A few examples will illustrate the application of the physical method of testing as an

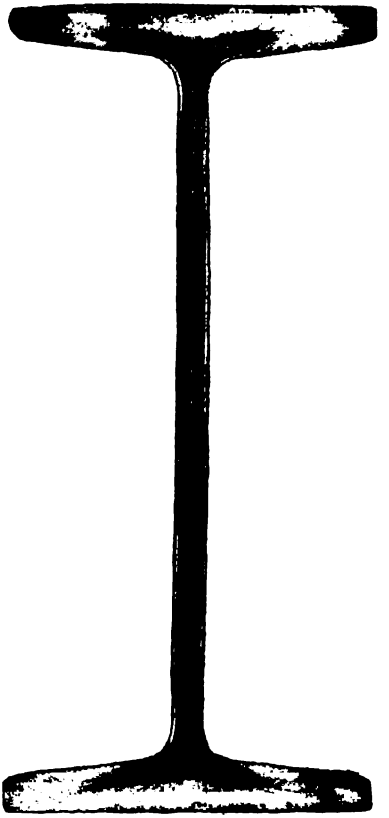


FIG. 91.—From the top of the ingot.

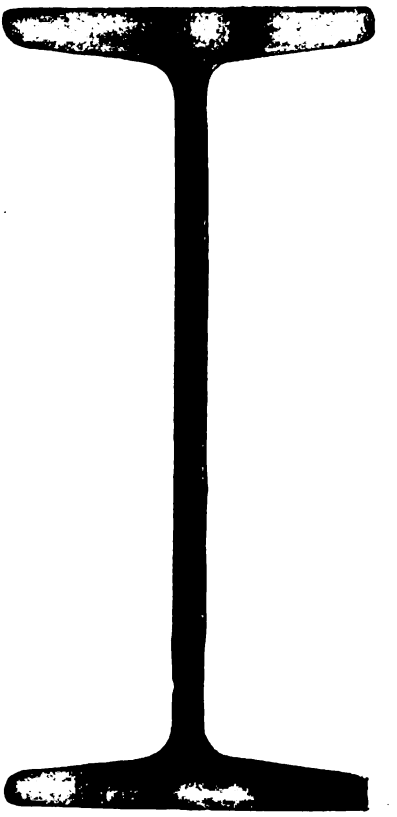


FIG. 92.—From the base of the ingot.

aid to the chemist not only in selecting his samples but also in forming an opinion as to the character of the material under examination.

Segregation in wrought iron and steel cannot be wholly overcome though with suitable precautions it can be greatly reduced.

It is important, therefore, for the steel mill to have a means of determining from time to time the amount of segregation in the ingots. To cut sections from the ingot itself for the purpose of making microscopical tests would be difficult and would interfere seriously with mill operations. An examination of pieces rolled from the top and from the bottom of the ingot answers the purpose.

If an ingot containing segregated material is rolled into any particular shape (angle-iron, beam, rail, plate, etc.) the zone of segregation appears in the rolled piece. The I-beams shown in Figs. 91 and 92 are rolled from the same basic-Bessemer ingot from

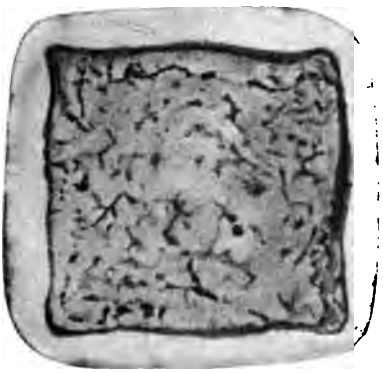


FIG. 93.—From the top of the ingot.

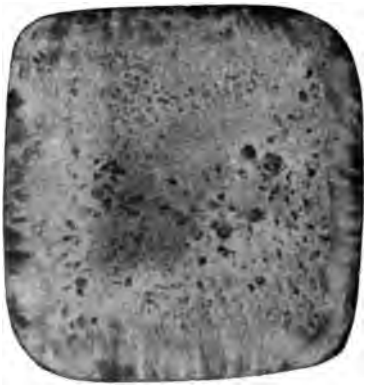


FIG. 94.—From the base of the ingot.

which the sections shown in Figs. 87 and 88 were taken. Figure 91 corresponds to the top of the ingot and Fig. 92 to the bottom. In the beam rolled from the top of the ingot the dark dividing band between the inner and outer zones is clearly marked while in the other beam no division is evident. The blow holes have disappeared. The agreement between the original ingot and the rolled material with respect to zone formation is clearly shown.

Figures 93 and 94 are made from basic-Bessemer ingot rolled out to small rods. Figure 93 represents in this case the top of the ingot, while Fig. 94 is from the lower end. The segregation phenomena are exactly similar to those just described.

TABLE VI

	Corresponding to top of ingot		Corresponding to bottom of ingot	
	Center, per cent	Edge, per cent	Center, per cent	Edge, per cent
Carbon	0.110	0.08	0.090	0.09
Manganese	0.520	0.50	0.480	0.52
Phosphorus	1.125	0.08	0.075	0.08

Here again the differences between the center and the edge of the piece rolled from the top of the ingot are considerable, while these differences almost disappear in the other pieces

FIG. 95.—Section of a connecting-rod screw.

These examples indicate that in order to get an idea of the nature of the segregation in the ingot, it is not enough to take a section from a piece rolled from one end of the ingot, but it is absolutely necessary to have sections corresponding to both ends, and in many cases to have a section representing the center of the ingot as well.

Figure 95 shows the etched surface of a broken connecting-rod. The inner core *K* contains numerous dark spots rich in small, non-metallic inclusions. The bright outer zone is crossed by dark lines perpendicular to the sides of the quadrangle which bounds the inner zone. These come from the blow holes which were perpendicular to the edges of the original ingot and were closed up during the rolling. The four-cornered cross-section of the inner zone shows that the ingot from which the rod was made was quadrangular in cross-section.

Analyses gave these values:

TABLE VII

	Inner zone, per cent	Outer zone, per cent
Carbon	0.11	0.09
Phosphorus	0.08	0.05
Sulfur	0.08	0.04
Manganese	0.72	0.70
Silicon	Trace	Trace
Copper	0.02	0.02
Nickel	0.07	0.07

FIG. 96.—Square bar of basic-Bessemer steel.

Carbon, phosphorus and sulfur have segregated in the inner zone.

Figure 96 is the polished cross-section of a square bar of basic-Bessemer steel. The section shows in the dark colored inner zone numerous small non-metallic inclusions evidently of a sulfidic character. Analyses of the two zones gave:

TABLE VIII

	Inner zone, per cent	Outer zone, per cent
Carbon	0.092	0.096
Manganese	0.410	0.380
Silicon	0.012	0.014
Phosphorus	0.060	0.050
Sulfur	0.072	0.030
Copper	0.074	0.050
Nitrogen	0.010	0.009

Besides the slight segregation of phosphorus there is a much larger sulfur segregation in the inner zone.

If, in the cases just cited, the samples for analysis had not been taken by planing across the entire section p. 423, but by boring, it would have been quite possible to obtain unreliable results even if holes had been drilled all the way through the metal. If, for example, a round rod is drilled as indicated by *I*, Fig. 97 the drillings do not correspond to the average composition as would those made by planing. The relative position of the holes has an influence on the values obtained. (See points *I* and *II* in Fig. 97.) More drillings from the unsegregated outer zone would be made by a hole at *I* than at *II*. The drillings from hole *I* are therefore poorer in phosphorus and sulfur than those from hole *II*.

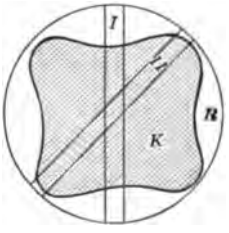


FIG. 97.

These facts hold not only for round or square pieces, but also for those of any other shape if segregation into any inner and outer zone has taken place in the ingot.

Even with correct sampling, analytical differences may occur

under certain conditions. Assume, for example, that the material of which the bar or other piece consists was sampled correctly by the shipper by planing over the whole cross-section and a phosphorus determination made. The sample contained "a" per cent phosphorus. The rod was then turned down by the purchaser and used for construction work. Because of a break, the finished product was analyzed for phosphorus. In this case too the sample was taken correctly by planing. The average phosphorus content would have been greater in this case if the original bar contained a core rich in phosphorus, as the outer zone, low in phosphorus, would have been removed by turning. Microscopic tests would indicate the difference between the original bar and the finished product.

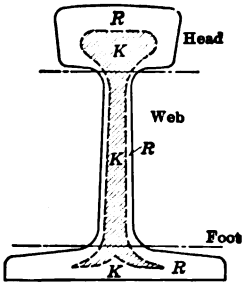


FIG. 98.

As stated on p. 381 and illustrated in Fig. 91, the segregation zone goes through the various processes of mechanical treatment, rolling, forging, etc., without coming to the surface of the piece. Because of the flowing of the material of the outer zone on rolling, very considerable changes in the relative areas and shapes of the inner and outer zones may take place. The dark inner zone forms a much larger proportion of the total area in the web of the I-beam (Fig. 91) than in the flanges. The same thing is true in the case of rails and other rolled forms. Figure 98 is a drawing of an etched rail section. The inner zone is cross-hatched. The ratio between the areas of the inner and outer zones in the different parts of the rail were as follows:

TABLE IX

	Proportional area of inner zone, *K*, per cent	Proportional area of outer zone, *R*, per cent
In head of rail	32.1	67.9
In web of rail	63.4	36.6
In foot of rail	14.4	85.6

Chemical analysis gave the following results:

TABLE X

	Inner zone *K*, per cent	Outer zone *R*, per cent
Phosphorus	0.127	0.063
Sulfur	0.060	0.023
Manganese	0.550	0.500

The differences in chemical composition between the inner zone *K* and the outer zone *R* are quite marked. A representative

FIG. 99.—Cross-section of a mine rail.

sample for analysis can be obtained only by planing over the entire cross-section. Planing part of the section (for example only the upper half) would give incorrect values because of the uneven distribution of the sulfur and phosphorus in the final product. (See Table IX.)

A similar case of marked segregation is illustrated in Fig. 99 the cross-section of a mine rail. Three distinct zones are noticeable.

(*a*) A narrow rim around the outer edge of the section, colored dark by the etching reagent.

(*b*) An intermediate zone R_2 which stays bright after etching.

(*c*) An inner zone made very dark by etching and containing many small, non-metallic inclusions, probably due to deoxidation.

Chemical analysis gave:

TABLE XI

	Inner zone, K, per cent	Outer zones, R_1 and R_2, per cent
Phosphorus	0.158	0.115
Sulfur	0.064	0.042

Owing to the peculiar distribution of the zones which are rich in phosphorus, the average phosphorus content in the two outer zones $R_1 + R_2$ is also high.

Sheet iron, boiler plate, hoop iron and other flat forms often give difficulty in sampling as the following example illustrates. A red-short boiler plate was analyzed for sulfur by several chemists. Samples of the steel were sent in sealed packages to the various laboratories, and the results returned varied from 0.067 per cent, to 0.24 per cent sulfur. The differences were altogether greater than possible differences due to different methods of analysis or to experimental errors.

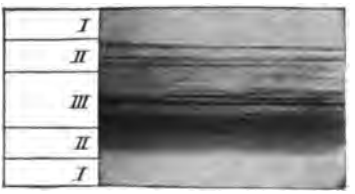


FIG. 100.—Red short boiler plate.

Metallographic study explained the situation at once, showing not only the reasons for the analytical differences but also the cause of the original difficulty with the boiler. Marked zone formation had taken place due to segregation as shown in Fig. 100. After the segregated areas had been located, borings were taken from the different zones and gave on analysis the following sulfur values.

Sample taken from	Sulfur, per cent
Zone *I*	0.067
Zone *II*	0.201
Zone *III*	0.240

The samples submitted to the different laboratories were evidently incorrectly taken by drilling or planing in different places so that one laboratory had samples from the low sulfur zone *I*, the second from the area *II*, which was somewhat richer in sulfur, and a third from the most segregated area *III*. An average value could be obtained only by planing over the entire cross-section of the specimen and even then the macroscopic results would be of greater value than those obtained by analysis.

Many more examples of segregation in rolled or shaped material might be cited but the illustrations given will serve to indicate the usefulness of macroscopic study, both as an aid in getting samples which are actually representative of the material under inspection and as a means of getting independently of chemical analysis or physical testing, extremely useful information concerning the properties of the metal.

Before the subject of steel ingots and the rolled or wrought material made from them is left, a brief reference to *Stead's reagent* must be made. This reagent is used for the purpose of detecting phosphorus segregations in steel and is prepared as follows:

Cupric chloride	10 g.
Magnesium chloride	40 g.
Hydrochloric acid	20 c.c.
Alcohol, sufficient to make	1,000 c.c.

Cover the specimen with a thin layer of the reagent, but do not immerse it. Shake off the layer of liquid after it has acted for 1 min., and replace it with a fresh portion of the acid mixture. Repeat the operation until the desired results have been obtained, then wash first with boiling water and finally with alcohol. Copper deposits on the phosphorus-free areas first, and by successive treatments it is possible to determine with a considerable degree of accuracy the relative phosphorus concentrations in different areas of the specimen. If the phosphorus is highly localized at any point, the segregated spots will stay bright even after ten treatments with the etching material.

CHAPTER XXVI

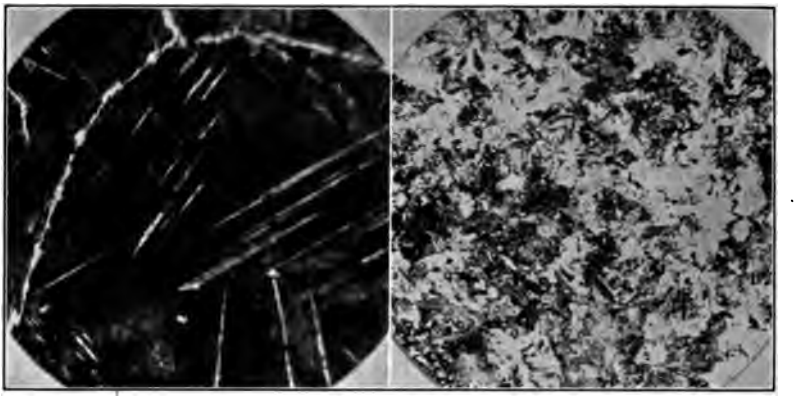
GENERAL STUDY OF STEEL WITH THE MICROSCOPE

The general features of the steel specimen, segregation of phosphorus, sulfide inclusions and the like may be studied without the use of the microscope, but the exceedingly important changes due to tempering, annealing and other operations, included under the general head of heat treatment, can be followed only with the microscope. A complete review of all the changes produced by varying the rates of heating and cooling and the microscopic appearances of the resulting steels, would cover almost the whole field of steel metallography. Therefore it will be possible to select only a limited number of examples to show the ways in which the microscope may be used to aid the chemist in his professional work.

Tempering.—Tempering is the term used to indicate the softening of hardened steel (martensite or austenite, p. 357) by reheating at suitable temperatures. The higher the reheating temperature, the softer is the material due to the change from martensite to troostite and finally to sorbite. In the lower ranges of tempering, the microscope shows the gradual increase in the amount of troostite and when the temperature reaches 400°C. the change to troostite should be complete. From 400 to 600°C. sorbite in increasing amounts should be found. Since the properties of the two constituents differ so materially, the microscope makes it possible to determine much more accurately than could be done by chemical analysis, whether or not the material has been treated to give the properties necessary for the purpose for which it is to be used.

Annealing.—Steel is annealed in order to relieve strains produced by sudden chilling or by working, or it may be done with the idea of refining a steel in which the crystal grains are too large to give to the material its best physical properties. In order that annealing may be effective, the material must be heated above its critical range. If it has not been so heated the microscope will show crystal grains of the same size as before

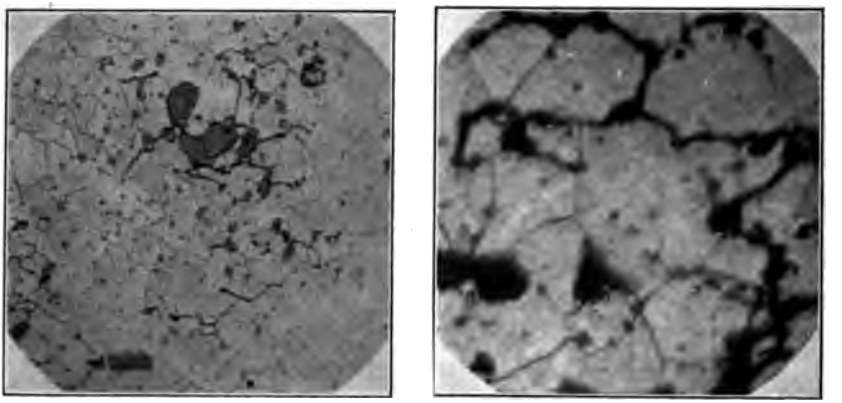
the annealing operation. The greatest dangers in annealing, however, and the two conditions most readily detected are **overheating** and **burning**. The former occurs when the an-



A *B*

FIG. 101.—*A* shows overheated steel and *B* fine grained structure.

nealing operation is carried out at too high a temperature, and leads to an abnormal growth of the crystal grains and a conse-



A = 100 × *B* = 300 ×

FIG. 102.—Burned low carbon steel. (*Johnson.*)

quent weakening of the material. The microscopic appearance of an overheated steel in contrast to a properly annealed steel is shown in Fig. 101. *A* shows the very coarse structure

characteristic of overheated steel, while *B* shows the fine grained structure of good steel. Burning, a much more serious defect, is caused by raising, the annealing temperature almost to the fusion point of the metal (above FeB, Fig. 59, p. 356). It causes a marked increase in the size of the grains, but in addition, as will be seen in Fig. 102, there is a marked thickening and darkening of the grain boundaries. This may be due to an escape of dissolved gases, to oxide formation or to segregations of molten phosphide. In the latter case the burned structure is most clearly developed by the use of Stead's phosphide reagent (p. 389).

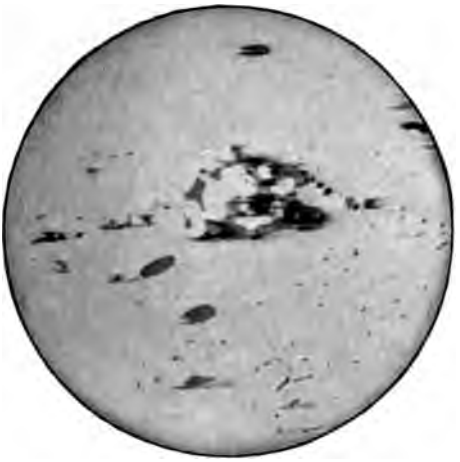


FIG. 103.—Sulfide inclusions.

Other applications of the microscope to the general study of steel are common. Slag or sulphide inclusions, Fig. 103, too small to be detected by macroscopic examination become evident, irregular distribution of troostite, martensite and sorbite areas due to uneven tempering, Fig. 104, may be detected and in many other similar cases the microscope will be found of great value in the study of suspected material.

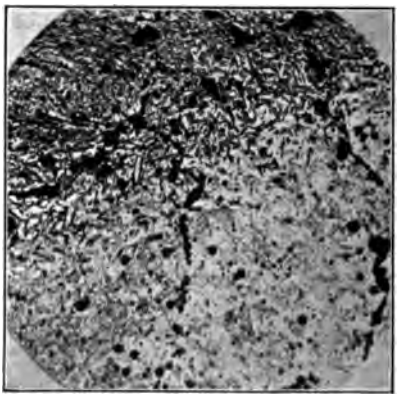


FIG. 104.—Sorbite, martensite and troostite. 100 ×. (*Homerberg.*)

Cold-worked Material.—Mechanical work, such as rolling, forging or pressing which is done above the critical temperature, Fig. 59, p. 356 (about 700 to 850°C.) produces changes in the

shape of the material, but any changes in the internal structure of the metal will be more or less completely overcome during the cooling through the critical range, especially if the rate of cooling is slow, as is commonly the case. The chief advantage of the microscope in the case of such "hot-worked" material is in determining the size of the crystal grains and therefore in forming an estimate of the finishing temperature (that temperature at which working stops). It is generally true that the higher the finishing temperature above the critical temperature, the coarser and therefore the less satisfactory will be the resulting

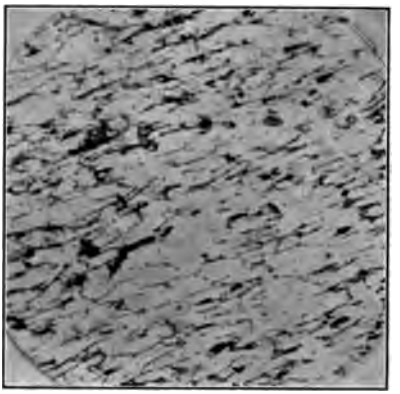


FIG. 105.—Cold drawn steel. 100 ×. (*Homerberg.*)

structure. If the work is carried on at temperatures lower than about 700°C., and especially if the material is rolled or drawn at ordinary temperatures, the operation is known as "cold working." Such material is always found in a more or less strained condition. Cold work may be done intentionally, or it may be done by accident if the operations of rolling, drawing and the like are not stopped above the critical range. In either case the microscope may be used to great advantage, as indicated in the photograph, Fig. 105, which illustrates a piece of steel subjected to severe strain in the cold condition. The distribution of the crystal grains in lines parallel to the direction of the pull is plainly evident. The material has a somewhat

higher tensile strength than unstrained steel but a greatly decreased ductility and is especially liable to fracture when it is subjected to sudden shock. The condition of "strain hardness" (see p. 458) may be relieved by suitable annealing. If the strain hardness has been wholly removed, the steel should show regularly formed crystals with no evidence of elongated grains so that by observing the extent to which the distorted grains have been restored to their normal shape and size, the effectiveness of the annealing may be determined. Strain hardening is often produced unintentionally in various ways, as for example, in the hammering of rivets after they have become too cold to allow for the readjustment of the crystal shape after the distortion of rivetting. It is often necessary to force the steel parts of a building or bridge into place by the use of the

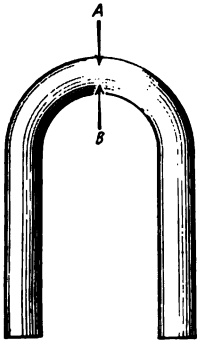


FIG. 106.

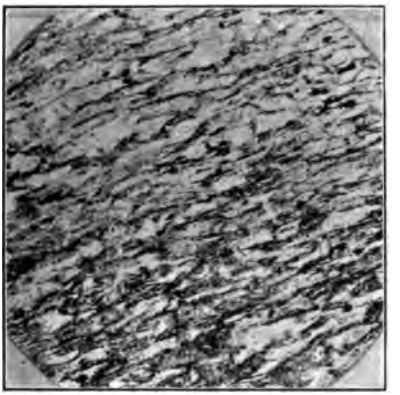


FIG. 107.—Steel under tension. (*A* in Fig. 106.) (*Homerberg.*)

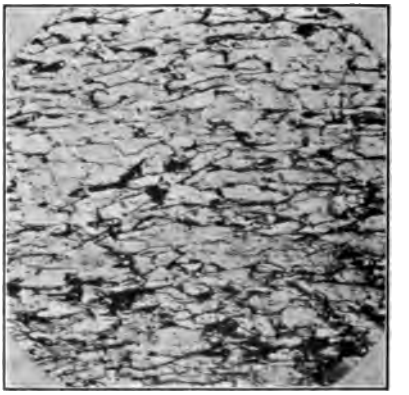


FIG. 108.—Steel under compression. (*B* in Fig. 106.) (*Homerberg.*)

sledge hammer. In such cases cold work is done, and may be the cause of brittleness leading to serious consequences later. Difficulties of this sort could not be controlled by microscopic examination, but if accidents occur under similar conditions it is often possible to determine the cause much more surely by the micro-

scope than in any other way. Figures 107 and 108 are photographs taken at the points *A* and *B* of the bent steel rod indicated in the sketch, Fig. 106. *A* illustrates the effect of tension while *B* shows the results of cold compression. Such distorted material is often found at the edge of a punched rivet hole, and not infrequently the resulting brittleness is great enough to cause cracking of the material.

Case-hardened Material.—It is often necessary to treat a piece of steel in such a way that a hard outer layer will be formed around a soft core. This operation of case-hardening produces a layer effect, which makes the question of adequate sampling a most difficult one. The outer case which is much richer in carbon than the core may have a thickness of several millimeters, and if the material has been quenched, as is often the case, it will be extremely hard. If such a piece is to be analyzed, it must first be annealed in order to get any sample at all. Special care must be taken to prevent surface oxidation during the annealing with a consequent loss of carbon. The annealing time, therefore, is made as short as possible (about ¼ hr.), and the annealing temperature is also kept as low as possible (750 to 800°C.). If the specimen in question is ordinary carbon steel it may be quenched in water after the furnace temperature has fallen below 700° as hardening does not take place below the pearlite point.

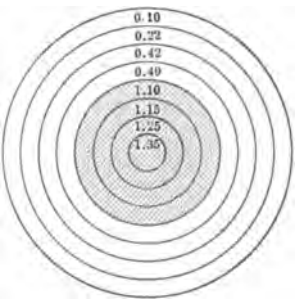


FIG. 109.

If the annealing furnace is kept at a high temperature (1,000° or higher) and the time is unduly prolonged (several hours for example) a marked diffusion of the carbon into the low-carbon area takes place. The chemical and microscopical study then gives a wrong idea of the original distribution of the carbon in the sample. The following illustration shows how great this change can be.

Arnold and M. Williams[1] fitted a piece of steel with 1.78 per cent carbon into a cylinder of iron nearly free from carbon and heated 10 hr. in a vacuum at 1,000°. Figure 109 shows the

[1] *J. Iron and Steel Institute*, **1899**, 85.

distribution of the carbon after the heating. The dark inner part is the steel core and the outer part the iron shell. The circles represent the different layers which were removed successively and analyzed for carbon. The inscribed percentages show clearly the gradual diffusion of the carbon from the steel to the soft iron. Metallographic examination shows with great sharpness the depth of the carbonized layer and gives at least an approximate idea of the increase in carbon content.

FIG. 110.—Section of case-hardened axle-bearing. 4 ×.

Figure 110 shows with fourfold magnification the cross-section of a small case-hardened axle-bearing. The thickness of the carbon-rich layer *R* (light in the photograph) was about 0.55 mm. The outer zone *R* contained 0.95 per cent carbon while the core *K* (dark in the photograph) had only about 0.1 per cent. There was a fairly sharp transition from the high-carbon content of zone *R* to the low-carbon zone *K* as shown in Fig. 111 with a magnification of 117 diameters.

When samples are taken of case-hardened material, it is much more satisfactory to determine the depth of the case by microscopic examination and then plane or turn down the material to the desired depth, analyzing the case and the core separately, than it is to attempt to get a representative sample by drilling or planing the whole specimen.

Decarbonizing.—Long heating in an oxygen-rich atmosphere causes a change which is exactly the reverse of that just described, and is of almost equal importance both with regard to getting representative samples of the material for analysis and in determining its properties. The outer surface (and sometimes a layer extending some distance into the material) becomes decarbonized and changes from a very hard, brittle material to almost pure iron, which is characterized by its softness. The decar-

bonizing effect is never produced intentionally, but often occurs in steel which has been annealed either for too long a time or at too high a temperature. Figure 112 shows a piece of cast steel in natural size, which was decarbonized by too long annealing.

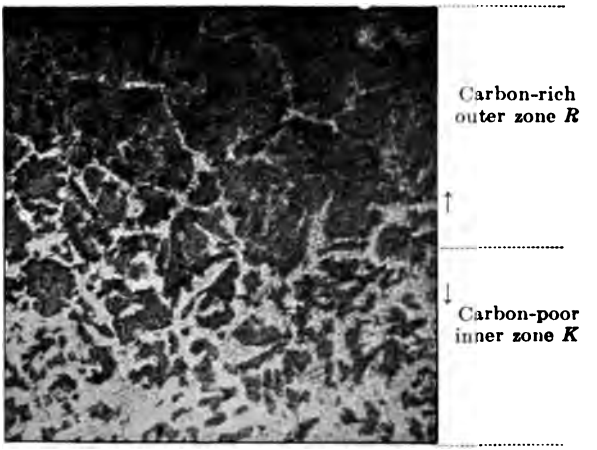


FIG. 111.—Transition from inner to outer zone. 117 ×.

Etching with copper ammonium chloride causes a darkening of the core which is rich in carbon and thus gives a good idea of the depth of the decarbonization. The transition from the decarbonized outer layer to the carbon-rich inner zone is shown in Fig.

FIG. 112.—Steel casting superficially decarbonized by too long annealing.

113 with a magnification of 117 diameters. Microscopic examination gives a clear idea of the amount of decarbonization without the necessity of analysis. Similar phenomena play a very undesirable part in the behavior of tool steel. The decarboniza-

tion is often confined to a very thin layer or occurs locally. If this partial decarbonization takes place exactly where hardness is required, difficulties arise which can be overcome only if the

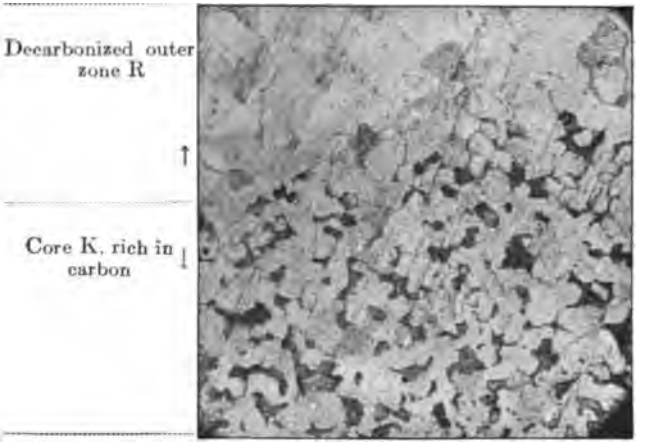


FIG. 113.—Transition from outer to inner zone. 117 ×.

cause is known. A chemical analysis without a previous metallographic examination would be valueless in cases of this sort, where accidental and unexpected local changes in the chemical composition of the steel have occurred.

CHAPTER XXVII

IRON

Reference to the iron-carbon diagram(Fig. 59, p. 356) shows that the range including pig and cast iron extends from 1.7 to 4 or 5 per cent C. The cementite which separates along the line *CE* is so readily decomposed on cooling that three classes of iron are recognized, depending on the cooling rate and on the presence of constituents other than carbon. These classes are known from their general appearance as **white iron, gray iron** and **mottled iron,** the last a combination of the other two.

White iron results from the rapid cooling (quenching or chill casting) of the metal, and has the white fracture and the hard, brittle characteristics of cementite. Its formation is favored by the presence of manganese and sulfur and the absence of silicon. White iron is too hard and brittle for common use, and is seldom found in small castings. It is often produced intentionally, however, as a hard facing on a softer core as, for example, in the casting of car wheels or the surfacing of rolls. In cases of this sort the white iron is associated with mottled and gray iron and the microscope is of great value in determing the thickness of the chilled (white iron) layer. The characteristics of **chilled castings** are illustrated in the following figures. Figure 114 shows the casting in natural size, and illustrates clearly the transition from the white iron of the chilled surface α, through the mottled iron section β and into the final gray form γ. The three zones are shown in detail in Figs. 115, 116, 117, Figure 115 is a section from the white border, magnified 350 diameters. The white areas are cementite, and the dark masses, pearlite. Figure 116 shows the transition zone of mottled iron, in which, in addition to the cementite and pearlite, small patches of graphite occur. Figure 117 corresponds to the gray part of the casting, and shows large masses of graphite with the pearlite and almost no cementite.

An average analysis over the whole cross-section (α = white edge, β = transition zone and γ = gray iron core) would be of no value in this case. It is sometimes useful to know the composition of the individual layers α, β and γ, and to get this, samples

for analysis should be taken from each of the zones. After the depth of the layers has been determined by the microscope,

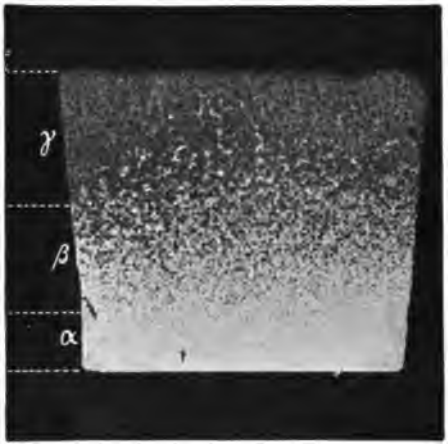


FIG. 114.—Chilled casting. 1 ×.

shavings for analysis should be taken from the gray iron first, either by planing or by boring and in the same way from mottled

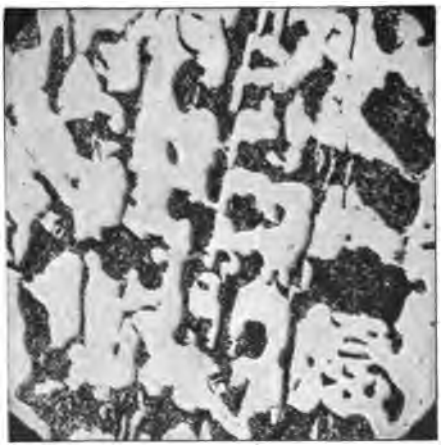


FIG. 115.—Section made from white border, α, in Fig. 114. 350 ×.

iron. The thin layer of white iron which is left and which cannot be machined is then broken to pieces.

In addition to these differences in physical properties and metallographic structure which are due chiefly to variations in the

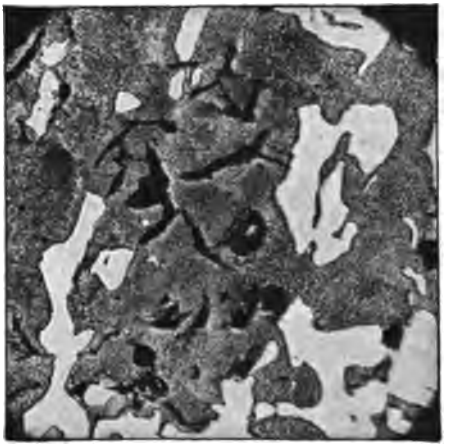


FIG. 116.—Section taken at the transition zone, β. 350 ×.

cooling rate, several other difficulties sometimes occur in the sampling and inspection of white iron.

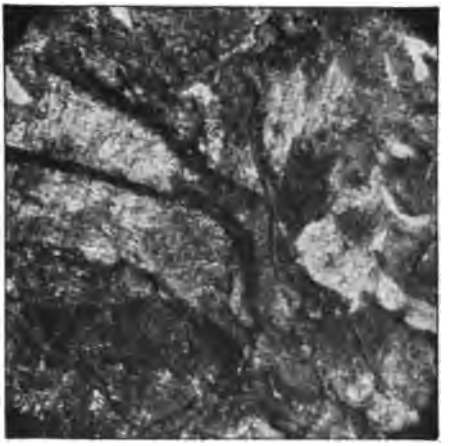


FIG. 117.—Taken at the part γ. 350 ×.

Formation of Globules and Nodules.—It happens not infrequently that in pig iron and in large castings, well formed

globules or nodules, sometimes as large as a walnut and quite different from the rest of the metal in composition, separate from the matrix and remain inclosed in the pig or casting. Sometimes they are in close contact with the metal, at other times they are contained in cavities in the casting. These inclusions are always much higher in phosphorus than the matrix, but lower in silicon. Platz studied the composition of globules of this sort and found the following values:

TABLE XIII.—ANALYSES OF GLOBULES AND NODULES ACCORDING TO PLATZ

	Gray iron with white edge			Mottled iron			Mottled pig iron	
	Globules, per cent		Matrix, per cent	Globules, per cent	Nodules, per cent	Matrix, per cent	Globules, per cent	Matrix, per cent
	Large	Small						
Silicon.....	0.58	0.54	0.98	0.58	0.52	0.86	0.48	0.85
Phosphorus..	1.82	2.38	0.29	1.44	0.66	0.30	1.65	0.40
Manganese..	1.17	1.22	0.72	1.02	0.78	0.70	2.25	1.92

Because of their high phosphorus content, the globules have a much lower melting point than the matrix. When the matrix solidifies, the still-liquid alloy (phosphide eutectic) is pressed into the contraction cavities where it hardens in the shape of spherical masses.

Crystal Formation in Cavities.—The pigs of low-spiegel, puddle iron with 5 to 7 per cent manganese often contain internal cavities filled with well-developed, leaf-like crystals. When the pig is first broken these crystal leaves have a mirror surface, which on contact with the air soon becomes coated with a layer of oxide, brownish yellow to deep blue in color and so thin that it can be neglected as far as its effect on the analytical results is concerned. The chemical study of the crystals and the matrix always shows a marked difference in the composition of the two.

Separations on the Outer Surface of White Iron.—It is well known that when molten white iron is allowed to stand, small masses of metal, which are very different from the matrix in composition separate. Ledebur found lumps weighing more than 500 g. in white pig iron rich in manganese and phosphorus.

The table shows that these lumps are largely manganese sulfide. They solidify while the matrix is still liquid.

TABLE XIV.—ANALYSES OF THE MASSES SEPARATING ON THE SURFACE OF WHITE IRON

	Manganese	Sulfur
The lumps contained.....	up to 9 per cent	up to 3 per cent
The matrix contained.....	3 to 4 per cent	0.3 per cent at most

Effect of Remelting on the Chemical Composition of White Iron.—It would not be correct to base the composition of the original white iron on the composition of the casting made from it because the iron changes its composition very materially when it is remelted. It is also true that the method of melting, whether in the crucible, open hearth or cupola furnace, has a marked influence on the final composition.

After three remeltings of white iron in graphite crucibles (3 parts graphite to 3.25 parts clay) the following changes in composition were determined:

TABLE XV.—ANALYSES BY MÜLLER

	Carbon, per cent	Silicon, per cent	Manganese, per cent
Before remelting.....	3.59	0.07	2.04
After first remelting.....	3.71	0.57	1.91
After second remelting.....	3.77	0.76	1.85
After third remelting.....	3.63	1.07	1.86

The original white iron showed, after each remelting, a strong separation of graphite with a simultaneous increase in silicon content and decrease in manganese content. After four remeltings the white iron had been changed completely to gray iron. Unfortunately the corresponding graphite determinations were not carried out.

A sample of **spiegel** with about 12 per cent manganese was melted in a graphite crucible, and allowed to cool slowly in the

furnace. After breaking, the lower half showed a brilliant white fracture while the upper half gave a dull gray fracture. Microscopic study and chemical analysis showed that in the upper half a marked separation of graphite had occurred while the lower half had remained white. The total carbon content of the upper half was increased and the manganese content was reduced throughout by about 2 per cent. (See Table XVI.)

TABLE XVI.—SPIEGELEISEN WITH 12 PER CENT MANGANESE AFTER MELTING IN A GRAPHITE CRUCIBLE

	Lower half, per cent	Upper half, per cent
Total carbon	5.43	5.19
Graphite	0.31	1.80
Combined carbon	5.12	3.39
Manganese	9.77	9.61
Silicon	0.94	0.88

Figure 118 (magnified 350 diameters) shows the structure of the lower white half *B*. Figure 119 (magnified 117 diameters) is taken from the upper gray half.

Influence of Heat on the Physical Composition of White Iron.—One of the important uses of white iron is as an intermediate product in the manufacture of malleable iron or malleable castings. If white pig iron is held for a long time at 700 to 800°C. (annealed), a decomposition of the iron carbide (cementite) and of the carbon rich solid solution (martensite) takes place. Carbon (temper carbon) and iron (ferrite) separate. The carbon which is formed under these conditions is chemically identical with graphite, and may be determined in the same way, but it gives to the iron physical properties which are markedly different from those of gray iron of the same chemical composition in which the graphite has separated in flakes instead of in the finally-divided form characteristic of temper carbon. Malleable iron has a tensile strength nearly twice that of gray iron of identical composition, and, instead of being brittle and susceptible to shock, is remarkably resistant to shock although not malleable in the sense in which the word is used in reference to steel. Decomposition does not take place uniformly throughout the

entire mass of the castings, but starts at individual centers and spreads out from them. In this process, the removal of the carbon (black heart) is not intended, but merely a change of

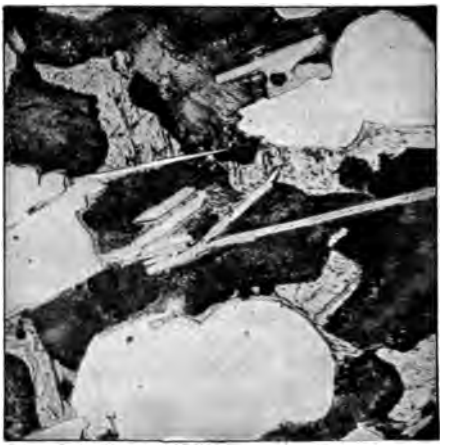


FIG. 118.—White spiegel. 350 ×.

the combined carbon into temper carbon. To what extent the desired result is obtained can be shown much more quickly

FIG. 119.—Gray spiegel. 117 ×

and surely by metallography than by chemical analysis. Figure 120 shows the effect of heating a piece of white pig iron for 108 hr. in wood charcoal. Large masses of temper carbon are

imbedded in the ferrite, and in addition cementite and pearlite are present.

FIG. 120.—Annealed malleable cast iron. 350 ×.

FIG. 121.—Malleable casting. 1 ×.

If the heating takes place in an atmosphere rich in oxygen (malleableizing), a simultaneous decarbonization takes place at

the surface and gradually works in toward the center. Figure 121 shows a casting treated in this way. It shows three distinct layers or zones with varying carbon content: (*a*) a zone at the

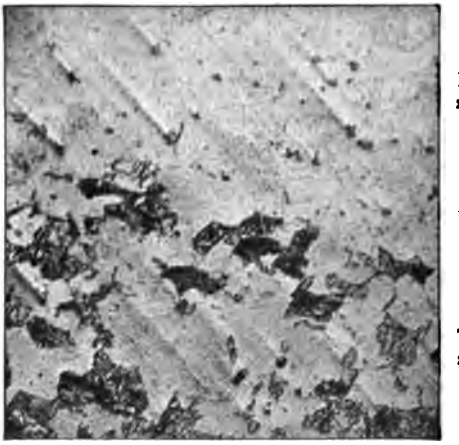


FIG. 122.—100 ×.

outside edges which is low in carbon (Fig. 122); (*b*) a transition zone richer in carbon (Fig. 122); (*c*) a zone at the center where temper carbon has deposited (Fig. 123).

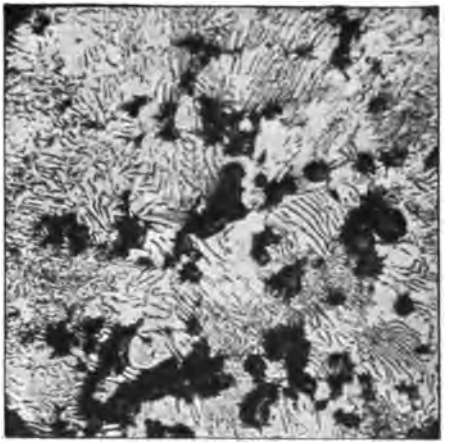


FIG. 123.—Central zone. 100 ×.

An average analysis is of no value in this case as it tells nothing of the way in which the carbon is distributed. It is best, in

all cases where an annealed piece is to be analyzed, to have the chemical analysis preceded by a metallographic examination. The chemical analysis of the malleable casting shown in Fig. 121 gave the following values:

TABLE XVII.—ANALYSIS OF A MALLEABLE CASTING

	Samples for analysis taken from the core *c*. (See Figs. 121, 122 and 123.) Per cent	Samples for analysis taken from the outer and from the transition zones[1] *a* and *b*. (See Figs. 121, 122 and 123.) Per cent
Total carbon	3.48	1.45
Temper carbon	2.60	0.96
Combined carbon	0.88	0.49
Silicon	0.65	0.66
Manganese	0.04	0.04
Phosphorus	0.083	0.085
Sulfur	0.22	0.224
Copper	0.21	0.22
Nickel	0.05	0.05

Many analyses indicating the separation of temper carbon have been published. In addition to the length of heating and the temperature, the chemical composition also has its influence on the separation of temper carbon.

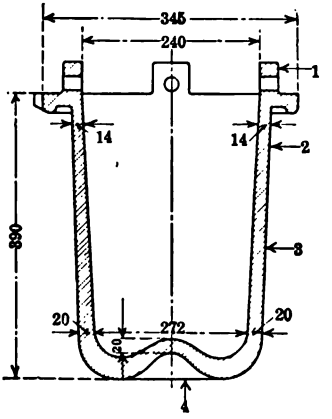


FIG. 124.

When the heating is done with coke or coal, the sulfur content usually increases because of the sulfur in the heating material. This increase takes place only in the outer layer. The percentages of manganese, silicon and phosphorus generally stay unchanged.

In the case of large pieces, if the heating temperature is not the same in all places or if the piece is not in good contact with the malleableizing agent (*e.g.*, ferric oxide) at all points, it may happen that some places are only partly malleableized or not malleableized at all. White, hard spots are left in the casting which become unpleasantly noticeable when the piece is machined. This con-

dition is sometimes found in an incompletely annealed wheel. In one spot it may show the characteristics of white iron (see Fig. 115) while in all other parts of the casting there is plenty of temper carbon. (See Fig. 71.)

Tempering is often produced unintentionally. Wüst[1] describes an interesting case of this accidental annealing. A gas retort of white iron (Fig. 124) was exposed for a long time to the action of furnace gases. The samples taken at the points marked 1 to 4 gave the following values:

TABLE XVIII

	Samples taken at			
	1	2	3	4
	Per cent	Per cent	Per cent	Per cent
Total carbon	3.39	3.33	3.04	0.50
Graphite and temper carbon	0.48	1.05	2.10	0.47
Combined carbon	2.91	2.28	0.94	0.03
Silicon	0.73	0.70	0.66	0.49
Manganese	0.48	0.46	0.44	0.39
Phosphorus	0.081	0.074	0.073	0.079
Sulfur	0.128	0.159	0.23	0.498
Oxygen	0.05	0.12	0.35	0.75

The shavings taken at 1 correspond to the original composition of the iron. A decided change in the chemical composition has been produced by the malleableizing effect of the flue gas. The greatest change has taken place at the bottom of the retort which was most directly exposed to the action of the hot gas. The total carbon grows less as the bottom is approached and the relative amount of temper carbon increases. The silicon content grows steadily smaller and there is an increase in both the sulfur and oxygen.

The effect of having an untrained workman take samples at random from the retort just described and sending them to different laboratories for a report on the composition of the retort material can be imagined. The result would be a series of analyses which would have no apparent connection with one another. Metallographic examination shows at once the reason for the varying results.

[1] F. WÜST, *Stahl u. Eisen*, **1903**, 1136.

CHAPTER XXVIII

GRAY IRON

Influence of the Cooling Rate on the Amount and Kind of Graphite in Cast Iron.—Ordinary iron castings are chiefly gray iron, which has been so named because of the gray color due to the separation of graphite in the massive form (Figs. 117 and 119), but as in the case of white iron (p. 399) the amount and kind of graphite which separates in gray iron depends largely on the rate of cooling.

Small castings will show a lower graphite content and a different distribution of the graphite than large castings made from the same iron. Even at the same cross-section, when the total carbon is uniform throughout, the graphite content on the outer edge of the casting, where the cooling is most rapid, is often less than in the center.

Since the amount and kind of graphite determines in large measure the mechanical properties of cast iron, it is often necessary to make analyses of different parts (edge, center, etc.).

Where the determination of graphite is the principal purpose of the analysis, it is better not to take the sample by planing or boring, but to cut out small pieces (sections or cubes) as shown in Fig. 125. In this way the sources of error in sampling and weighing, described in detail on p. 436, are eliminated without complicating the analytical work in any way.

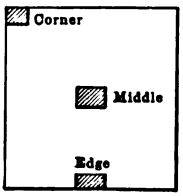


FIG. 125.

The following example[1] shows the effect of the nature of the cross-section on the graphite content. It happens, also, particularly with bars of greater cross-section, that there is less separation of graphite at the corners because of the quicker cooling there.

[1] E. HEYN, *Stahl u. Eisen*, **1906**, 1295.

Bars of various sizes ($\frac{7}{16}$ by $\frac{7}{16}$ to 6 in. by 6 in.) were cast in one piece as shown in Fig. 126. The average composition of the iron used was:

Total carbon	3.38	per cent
Silicon	2.51	per cent
Manganese	0.81	per cent
Phosphorus	0.56	per cent
Sulfur	0.095	per cent

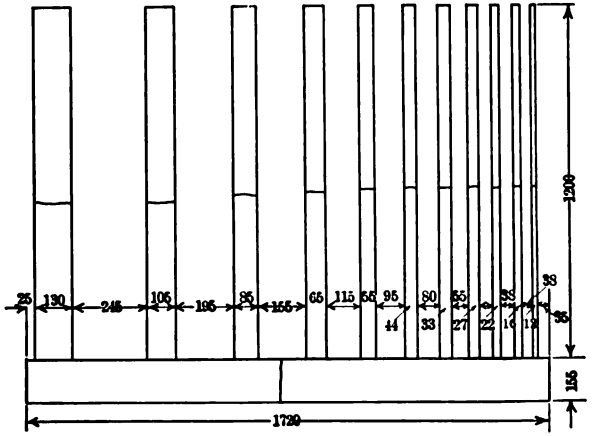


FIG. 126.—Dimensions in millimeters. Cf. Table XIX.

For the determination of graphite, samples were taken from the middle and from the edges as shown in Fig. 125. These samples were in the form of small pieces weighing about 2 g.

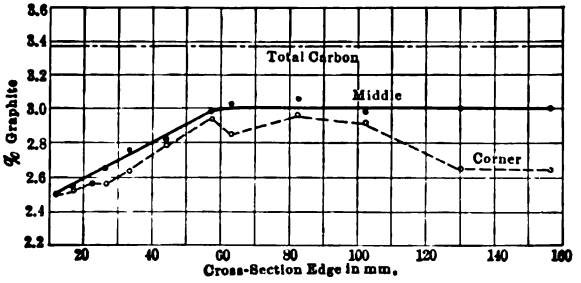


FIG. 127.

each. The results are given in the following table and shown graphically in Fig. 127.

Table XIX and Fig. 127 show that the graphite content is lowest in the center of the thinnest bars. It increases with increasing cross-section until a maximum is reached at 2⅝ by

TABLE XIX.—ANALYSES BY E. HEYN

Cross-section in mm.	Center of bar		Corner of bar	
	Per cent Graphite[1]	Graphite in per cent of total carbon	Per cent Graphite	Graphite in per cent of total carbon
155 × 155 (6 in. × 6 in.)	3.00	88.7	2.68	79.3
130 × 130 (5¼ in. × 5¼ in.)	3.00	88.7	2.68	79.3
105 × 105 (4¼ in. × 4¼ in.)	2.97	87.9	2.92	86.4
85 × 85 (3⅜ in. × 3⅜ in.)	3.06	90.5	2.95	87.2
65 × 65 (2⅝ in. × 2⅝ in.)	3.03	89.7	2.85	84.5
55 × 55 (2 1/16 in. × 2 1/16 in.)	2.98	88.2	2.94	86.9
44 × 44 (1¾ in. × 1¾ in.)	2.84	84.0	2.78	82.2
33 × 33 (1 5/16 in. × 1 5/16 in.)	2.77	82.0	2.62	77.5
27 × 27 (1 1/16 in. × 1 1/16 in.)	2.66	78.7	2.55	75.5
22 × 22 (⅞ in. × ⅞ in.)	2.55	75.5	2.55	75.5
16 × 16 (⅝ in. × ⅝ in.)	2.55	75.5	2.53	74.8
12 × 12 (1/16 in. × 1/16 in.)	2.50	74.0	Sample from the whole cross-section	

[1] The value given is in each case an average of from two to five separate determinations. Each determination was made on a new section.

2⅝ in. Investigation seems to indicate that under the conditions of the experiment (casting temperature, cooling rate, and silicon,

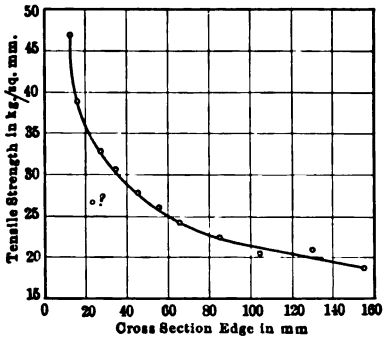


FIG. 128.

content of the iron) the cross-section 2⅝ by 2⅝ in. is large enough to allow the maximum graphite separation in the core

of the bar. At the corners of the larger bars, where the rate of cooling is considerably greater than in the center, the graphite content is much lower than in the center. With the small bars where the rate of cooling is approximately the same throughout, the differences in graphite content in different parts of the bar disappear.

That accidents also have considerable influence on the graphite separation at the corners of the bars is shown by the fairly wide variations in the analytical results.

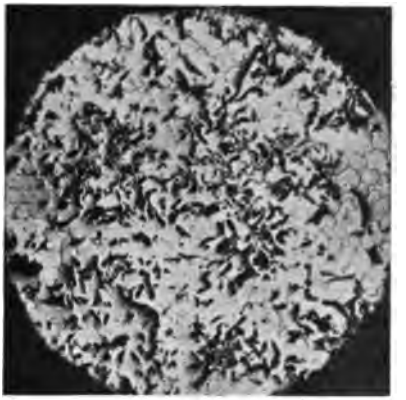
Not only the amount of graphite present but also the shape and size of the individual graphite plates may influence the physical properties of cast iron. Chemical analysis gives no indication of the size or shape of the graphite plates so that here again metallography must come to the aid of the chemist in explaining unusual conditions such as the differences in tensile strength of pieces of iron of identical chemical composition. The transverse strength of the bar shown in Fig. 126 is given in Fig. 128.

The transverse strength is greatest in the bar with the smallest cross-section. This decreases with increasing graphite content. In castings larger than 2⅝ by 2⅝ in. (the size at which the graphite content reaches its maximum and beyond which there is no change) there is a clearly marked decrease in the transverse strength with increasing size. Metallographic study explains these facts, as is shown in Fig. 129. The linear magnification is the same in all cases (117 diameters).

The photographs show very clearly that with increasing cross-section the size of the individual graphite crystals increases. The difference between the bar with the largest cross-section and the bar with the smallest cross-section is very marked. It is obvious that graphite plates of the length and size found in the bar with the largest cross-section would break up the continuity of the iron and so tend to weaken the tensile strength.

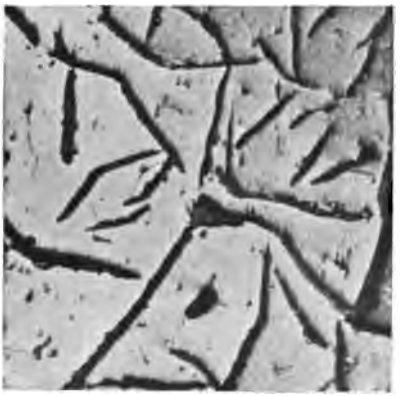
If the number of graphite plates occurring in 0.0016 sq. in. of surface in each bar is determined and these numbers are plotted as ordinates and the thicknesses of the bars are used as abscissas, the graphical results of the experiments described above are shown in Fig. 130. The number of graphite grains is greatest in the bars with the smallest cross-section and least in the largest ones. The number of graphite grains is greatest at the edges

FIG. 129.—Influence of thickness



Rod 7/16" × 7/16"

Rod 5/8" × 5/8"



Rod 6" × 6"

on the separation of graphite.

and corners in spite of the fact that the total graphite content is smallest at these points. The individual graphite crystals must be smaller in size in the small rods and at the corners of the larger ones than at the center of the larger bars. The results obtained by counting the individual graphite plates is in complete agreement with the results obtained by the metallographic study.

The following example illustrates very clearly the influence of the size of the bar on the graphite content. It is taken from an investigation by Jüngst.[1] Seven round bars from 3/16 to 2

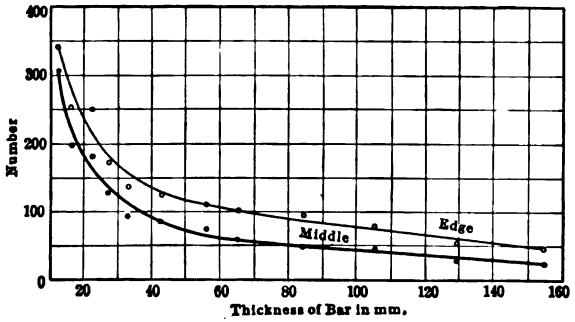


FIG. 130.

in. in diameter, cast at the same time from a mixture with 1.93 per cent silicon, 0.55 per cent manganese, 0.712 per cent phosphorus, and 0.090 per cent sulfur gave the following values:

ANALYSES BY JÜNGST

Diameter of bars	2 in.	1½ in.	1⅛ in.	¾ in.	9/16 in.	⅜ in.	3/16 in.
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Graphite	2.95	2.90	2.82	2.80	2.60	2.60	2.39
Combined carbon	0.42	0.50	0.60	0.60	0.72	0.78	0.99
Total carbon	3.37	3.40	3.42	3.40	3.32	3.38	3.38

The graphite content decreases regularly with increasing cross-section, the percentage of combined carbon increases and

[1] JÜNGST, *Stahl u. Eisen*, **1905**, p. 415.

the percentage of total carbon stays about the same. (See also Fig. 131.) Jüngst's results do not show any marked differences in graphite content between the edges and the middle of the specimen. The arrangement, number and size of the graphite plates are markedly different at the edges and at the core of the specimens.

The following example[1] is also interesting as it shows clearly that, especially with gray iron, the chemical analysis alone often fails to explain unusual behavior.

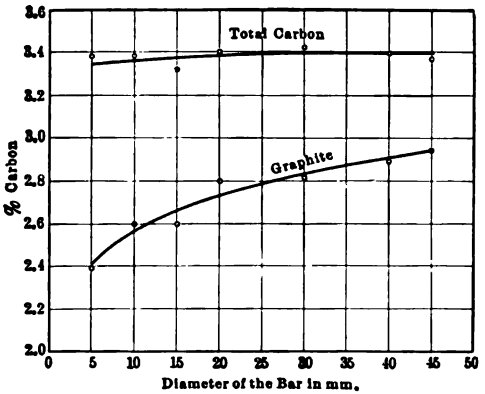


FIG. 131.

Cast iron rich in silicon was cast in a sand mold fitted with an iron bottom so that quenching experiments could be made. The mold was open at the top.

The fracture of the piece showed in the upper part (see Fig. 132) a very coarse grain with large graphite plates; the lower part of the specimen showed a sudden transition from the coarse to a fine structure in which the graphite plates were not visible. Chemical analysis of the upper and lower parts showed the composition of the two parts to be practically identical in spite of the marked difference in the appearance of the fracture. As a result of microscopic examination of the two parts, it was found that the coarse-grained, upper part was filled with long, large graphite leaves (Fig. 133) while the lower part showed the

[1] E. HEYN, *Stahl u. Eisen*, **1906**, p. 1295.

eutectic appearance and probably corresponded to a true graphite eutectic (Fig. 134). The mechanical properties of the two parts were very different.

Influence of Remelting on the Chemical Composition of Gray Iron.—The chemical composition of gray iron is changed by remelting, although, because of the greater stability of graphite as compared with cementite the changes in the physical properties are not nearly so marked as with white iron (p. 403). If a cupola furnace is used, in remelting the manganese is most readily oxidized, while the silicon, if the manganese is still high, will be affected but slightly. With high manganese content an increase in silicon may occur due to reduction of the slag. The silicon does not begin to burn until most of the manganese has been oxidized.

FIG. 132.—Fractured casting.

Carbon will stand a longer heating in the cupola furnace where the iron is in immediate contact with the hot coke, from which carbon can be taken as fast as it is used up, than in the reverberatory furnace where oxidation takes place quickly. With high manganese, the carbon content is likely to increase. Sulfur generally increases due to the presence of sulfur in the products of combustion, while the phosphorus content usually changes but little. Because of these various changes, the analysis of the original material from which

a casting is made may give only an approximate idea of the composition of the finished casting.

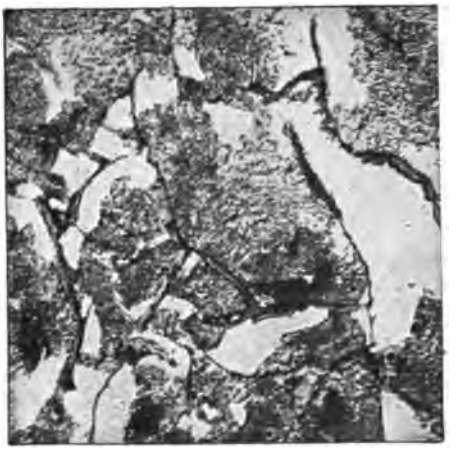


FIG. 133.—Upper half. 350 ×.

Influence of Annealing on Gray Iron.—Long-continued heating, at annealing temperatures (above 1,000°C.) and in an

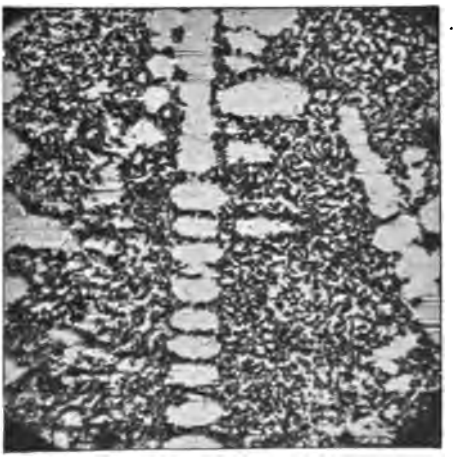


FIG. 134.—Lower half. 350 ×.

atmosphere rich in oxygen, can cause marked changes in the composition of gray iron, especially in the carbon content. An

iron casting containing 3.66 per cent carbon, of which 2.02 per cent was in the form of graphite, was annealed seven times at temperatures of about 1,000°, and at the end showed a drop in total carbon to 0.10 per cent and of graphite to 0.02 per cent. At the same time the sulfur had increased from 0.157 to 0.781 per cent In addition to the burning of the carbon under these conditions, it has been suggested that there is a slagging and segregation of the phosphorus. This is not at all impossible as the ternary eutectic (solid solution-carbide-phosphide) begins to melt at 950°.

Abnormal Formations in Gray Iron.—Growths of various sorts occur with gray iron much as they do with white iron, and their effects on the properties and methods of sampling are essentially the same. Globules or nodules varying in size from that of flax seed to masses one-fourth of an inch in diameter, may be formed on the surface of the iron. These masses differ widely from the main casting in composition and are always high in phosphorus. Well-defined crystals are sometimes found in cavities in the iron, and do not differ materially from the composition of the casting except that they are apt to be covered with a white coating, which is nearly pure silica and which would seriously influence the analysis of the sample if the crystal should happen to be included in the part selected. In depressions on the sides of the pig where the iron is in contact with the sand mold, mossy or asbestos-like growths of a yellowish white color are sometimes formed. These masses are found to be largely silica, though they often contain titanium and potassium. It has been suggested, as a possible reason for these masses, that a volatile silicon compound, probably silicon sulfide, is formed in pig iron and that when this compound comes in contact with the air, the sulfur burns to sulfur dioxide and the silicon forms silica which deposits on the colder walls of the pig or in the cavities.

These various irregularities in gray iron, both the normal changes due to remelting or annealing and the abnormal formations just described, indicate again the importance of preceding the chemical analysis by a metallographic examination, if possible, in order to be certain that the sample is homogeneous or, if it is not, to determine the nature and distribution of abnor-

mal deposits so that the chemist may know what his analysis really represents.

Disintegration of Cast Iron.—A more unusual cause of unsatisfactory results, the disregard of which may cause serious analytical errors, is the phenomenon of disintegration which often occurs under service conditions.

If, for example, a cast-iron water main lies for a number of years in contact with moist earth, a curious decomposition takes place. In certain spots on its surface the pipe, without losing its form, will change to a dull-gray mass so soft that it can be cut with a knife. The reason for this change has not been satisfactorily explained. Moisture is absolutely necessary, but whether the change is due chiefly to oxidation or to stray electric currents is still an open question. The following table shows the marked difference in composition between the corroded and uncorroded parts of the pipe.

TABLE XX

	In original casting, per cent	At the corroded spots, per cent
Total carbon	2.50	8.10
Silicon	2.66	9.30
Phosphorus	1.90	6.50
Iron	....	46.18

A similar effect is sometimes noticed with castings which have been exposed to heat. The cast-iron coils of a hot-water heater which had been exposed to the hot gases of the flame showed spots soft enough to be scraped off with a knife, especially at the threaded joints. Analysis of the soft material indicated clearly that it was a decomposition product of pig iron, the total carbon amounting to about 12 per cent, while the iron had dropped to about 39 per cent almost wholly combined with oxygen.

Figure 135 shows a badly corroded gray cast iron magnified to 350 diameters. The original graphite leaves appear light gray in contrast to the dark background.

Mottled Iron.—Since mottled iron is an intermediate product between white and gray irons, its sampling and analysis will be subject to the difficulties of both. It is especially likely to have

FIG. 135.—Decomposed cast iron. 350 ×.

the graphite and cementite masses, of which it is composed, irregularly distributed through the casting, so that the selection of a representative sample is one of much difficulty.

CHAPTER XXIX

SAMPLING OF IRON AND STEEL

Many of the difficulties connected with the selection of really representative samples of steel and iron have been mentioned in connection with the macroscopic and microscopic study of the metals, and suggestions have been made as to the best means of taking the samples in special cases. It may be of service to the analyst, however, to have this information assembled and to consider in a general way the methods used in the plant.

General Discussion of Sampling.—As a general rule for all metals that can be worked with a cutting tool, a better representative sample can be obtained by **planing** over the whole cross-section than by drilling, turning, etc., and when a metallographic study has preceded the chemical analysis, the shavings should be taken from the place adjoining that from which the specimen was taken for microscopical study. Figure 136 shows the method used in taking a sample from a steel rail.

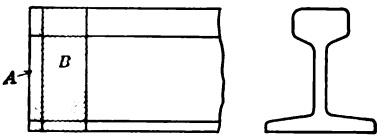


FIG. 136.—*A*. Section for metallographic study. The surface indicated by the cross-hatched line is ground, polished and etched. *B*. Shavings for analysis are obtained by planing the whole cross-section.

If marked irregularities are found by the microscopic study, it may be desirable under certain conditions to get samples from different parts of the specimen, in which case drilling, turning, etc., may be necessary. If merely an average analysis is required, however, planing of the whole surface is enough. In reporting a complete analysis, an exact statement should be given of the method of sampling, with an explanatory sketch if necessary. A sketch is indispensable if shavings have been taken from different parts of the specimen (core, outer zone, etc.).

Frequently, far too little care is taken with the purely mechanical part of taking samples, cleaning of the test specimen, plan-

ing and collecting samples, in spite of the fact that many serious errors can be introduced by careless work. The first requisite is naturally that the planer should be clean, that no shavings from previous tests are on it, and that all parts that come in contact with the specimen are free from oily, fatty, or soapy matter. Care must also be used to see that no oil or grease drops on the shavings already made.

Cleaning the Surface of the Test Piece.—Before taking a sample the surface of the piece must be examined carefully for external impurities and freed from any that may be found. First come the substances that adhere loosely, *e.g.*, sawdust from the packing, dirt, in case the specimen has lain on the ground, and similar impurities. These can often be removed by washing or by rubbing with a stiff brush or polishing cloth. Paint or shellac, letters, numbers, as well as rust spots, can be removed by means of a wire brush or, if necessary, by using a solvent for the paint (alcohol, ether, gasolene, kerosene), but only those solvents should be used which do not attack iron.

Surface coatings produced during the manufacture, *e.g.*, casting skin, forge scale, etc., adhere much more firmly than accidental impurities. If they cannot be removed by the steel wire brush, it is necessary to hammer, file, or rub with emery cloth. In such cases care should be taken not to remove large quantities of material.

Planing and Collecting the Shavings.—If the material is hard, the speed of the planer should not be too fast or the tension too high, as otherwise the shavings are apt to fly off and be lost, and there is the additional danger that pieces of the cutting tool may break off and contaminate the sample. If a piece of the cutting tool should fall into the sample and be weighed with it, incorrect results would be obtained without any reason apparent to the analyst. It is scarcely necessary to say that shavings which have fallen on the floor should not be used for analysis, as the chance of contaimination is too great. The greatest care should be used in the taking and collecting of samples in the shop.

In planing certain kinds of iron, the untrained workman is likely to pick up only the coarser shavings, leaving the finely powdered material, *e.g.*, graphite in cast iron or slag in wrought iron, on the bench or even blowing it away. The fact that very

serious errors can be introduced in this way will be shown on pp. 432 and 433.

To avoid losses, it is a good plan to place strong, glazed paper around the test piece, as shown in Fig 137. Then, if the cutting speed and tension are properly chosen so that the shavings do not spring away during the planing, the coarse shavings as well as the powdery material will fall into the paper and, after the removal of the test piece, may be shaken into a bottle without danger of loss.

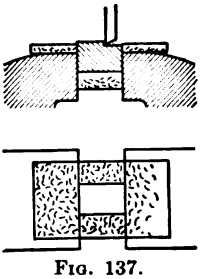


FIG. 137.

Annealing before Taking the Sample.— Hardened steel is often annealed before planing, to make it more easily machined. The annealing temperature in the case of carbon steel is such that it will be above the pearlite point (700°C with pure carbon steel). A quarter of an hour's annealing at 750 to 800°C followed by a slow cooling until the pearlite point is reached is enough. Below 600°C the cooling can take place quickly, for with carbon steels even quenching in water will not noticeably increase the hardness in this temperature range.

The following table may serve as an aid in determining the approximate temperature.[1]

Dull red heat	about 525° to 550°C
Dark red heat	about 700°
Dull cherry red	about 800°
Cherry red	about 900°
Bright cherry red	about 1000°
Dark orange	about 1100°
Bright orange	about 1200°
White heat	about 1300°
Bright white heat	about 1400°
Dazzling white heat	about 1600°

The heating can take place in an open charcoal fire. If it is done in a furnace (tube furnace, muffle furnace, etc.), it is advisable, in order to avoid the formation of forge scale with a consequent superficial decarbonization, to place pieces of

[1] Exact temperature measurements are made with a thermoelement. For details concerning these measurements, consult "The Measurement of High Temperatures" by G. K. Burgess and H. Le Chatelier.

charcoal before and behind the test piece. The air entering the furnace must then pass over hot carbon so that the oxygen is burned to carbon monoxide. The formation of forge scale can be prevented almost entirely in this simple way. The fear that superficial carbonization (cementation) of the test piece can be produced in this way by the carbon monoxide is unfounded. A very much longer time would be required to produce an appreciable cementation effect.[1]

It should be stated that the presence of certain elements in the steel, *e.g.*, manganese and nickel, causes a material lowering of the pearlite point. In such cases care must be taken in the cooling after annealing.

The Sampling of Materials which Cannot Be Machined.—Certain alloys and self-hardened steel cannot be machined with ordinary steel tools, even after annealing and slow cooling. White cast iron cannot be annealed because of the possible separation of temper carbon. In some cases special tool steel can be used (chrome-tungsten and similar alloy-steels). The usual precautions should be taken.

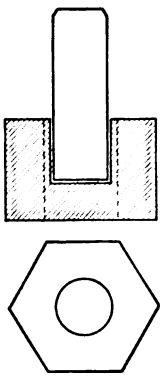


FIG. 138.

If, however, the material cannot be worked either with carbon steel or any of the special steels, it is necessary to knock off small pieces from different parts of the sample and to pulverize these pieces. This pulverizing can usually be done with a heavy hammer on a steel anvil. If the specimen is very large and heavy, a trip hammer is sometimes needed. To avoid scattering the small fragments, the sample should be wrapped in heavy linen cloth. If a trip hammer is used, a piece of iron should always be put between the test specimen and the hammer, to avoid possible injury to the machine. The broken pieces must be carefully cleaned to free them from linen fibers. The final powdering of the sample can be accomplished in a diamond mortar, the simplest form of which is shown in Fig. 138. The powder obtained after treatment of

[1] *cf.* BAUER, *cf Stahl u. Eisen*, **1909**, No. 18 has never succeeded in detecting by metallographic means the slightest trace of superficial carbonization after 15 min. annealing in contact with charcoal.

the larger lumps is coned up and quartered as in the usual way of sampling powdered ores.

Sampling of Material in Wire Form.—If the material is in the form of thick wire, it is beaten out on the anvil until it is in the form of thin sheets which can be cut with tin-smith's shears. Each wire is then cut into pieces of approximately the same length. For the final sample one or two of these shorter pieces from each coil are taken and, after thorough mixing, are cut into still smaller pieces for the final weighing. If there is doubt, or if the metallographic examination shows that the wires are not all alike, it is useless to take an average sample. In this case a number of small sections should be cut from the long wire and treated separately.

Sampling from the Molten Metal.—If it is a question of getting a representative sample from a large heat, it is safest to prepare two test ingots of 12 to 18 lb. in weight, one at the beginning and one at the end of the pour. With a very large heat, a third sample taken at the middle of the pour is advisable. The small ingots are cut through the center lengthwise as shown in Fig. 139. Samples are obtained by planing over the surface indicated by the shaded line in the figure. The shavings from the different ingots are united to make a single average sample. Under certain conditions it is better to analyze each ingot separately and take a mean of the results. It is possible to determine in this way whether or not segregation took place when the charge was in the molten condition, a thing which ought not to occur if the temperature is high enough.

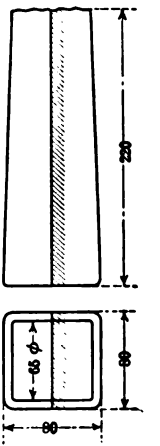


FIG. 139.

Instead of following the method just described, the United States Steel Corporation[1] takes a ladle test during each heat when approximately one-half of the metal has been poured. One of two types of sample mold is used to receive the melted metal. The first is a split mold, into which an ingot of about 1½ sq. in. cross section and 5¼ in. long is poured. The mold is pro-

[1] U. S. Steel Corp., "Methods for the Commercial Sampling and Analysis of Plain Carbon Steels."

vided with a flare, extending about 3 in. above the test bar, to serve as a shrink head for the molten metal. The second type is a cast-iron or steel ladle, 3¾ in. inside diameter at the top, 2½ in. at the bottom and ¾ in. deep. In both cases drillings are taken with a ¾-in. drill. The test bar from the mold of the first type is drilled at a point from 1 to 2½ in. from the bottom of the bar. The sample ingot of the second type is drilled from the bottom and to a depth not greater than 1 in. In both cases special care is taken to prevent scale from getting into the sample.

Sampling of Forged or Rolled Material.—If the shape of the piece to be analyzed allows, the sample for average composition should be taken by planing over the entire cross-section, not by boring or drilling. If, on the other hand, an average analysis is not needed, but the inspector wishes to know whether and to what extent segregation has taken place, or whether there are other irregularities in the chemical composition of the material, a metallographic examination should precede the sampling.

It would be wholly misleading, for instance, to take samples from a rolled rod by turning off the outer layer as indicated in Fig. 140. If zone formation has taken place, due to segregation, an analysis of turnings taken at the point *d* on the outer zone *R* would give an entirely false idea of the average composition of the bar, as that point represents the part of the bar in which segregation is least strongly marked. If now, in order to make a control analysis, the rod was turned down still more (*e* in Fig. 140) the analyst would find much higher percentages of phosphorus and sulfur, assuming that segregation had taken place as indicated.

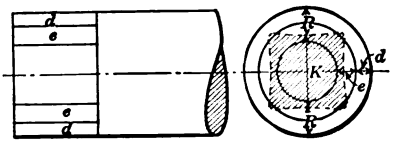


FIG. 140.

Rolled material is especially liable to contain segregated areas, as in the case of the round rod just referred to, but the nature and distribution of this segregated material varies so widely in different pieces that only one or two examples can be given to indicate the general nature of the difficulty and to

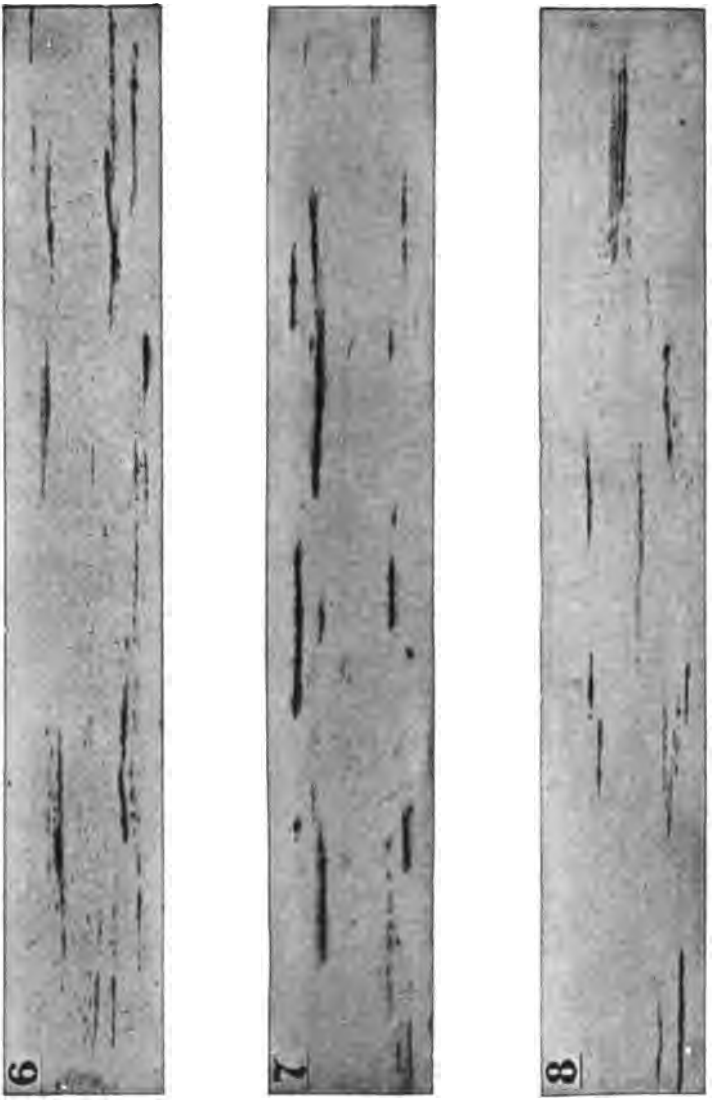


FIG. 141.—Sulfur prints on silk.

emphasize again the necessity of extreme care and judgment in the selection of the sample for analysis.

It frequently happens that the segregated areas are not sharply marked, but that smaller or larger segregated spots are irregularly distributed throughout the whole cross-section area. In this case there is no distinct division into an inner and outer zone. Figure 141 shows the sulfur prints on silk of three plates, in which the segregation stripes are irregularly distributed. Analysis gave:

TABLE XXI

Sample taken	Phosphorus, per cent	Sulfur, per cent
Over the whole cross-section	0.078	0.060
From the segregated streaks	0.183	0.101

In all these cases, representative samples could be taken by planing over the whole cross-section. In some cases, however, even shavings made by planing over the whole cross-section do not represent the average composition of the material.

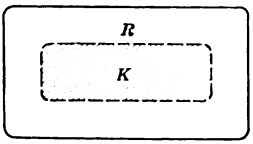


FIG. 142.

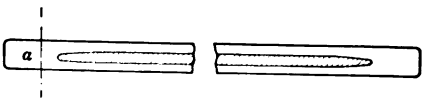


FIG. 143.

If a slab with an inner zone, K, like that indicated in Fig. 142, is rolled out to a plate, the inner zone tapers toward the ends and sides of the plate, as indicated in the sketch, Fig. 143, and in the photograph, Fig. 144.

If now, for the purpose of getting samples, the entire section is planed over at the place "a" in Fig. 143 the analysis will not show the true average composition of the material in spite of the apparently correct sampling, because the shavings really represent only the outer zone R.

Analysis of a plate with a tapering inner zone like that shown in Fig. 144 gave the values:

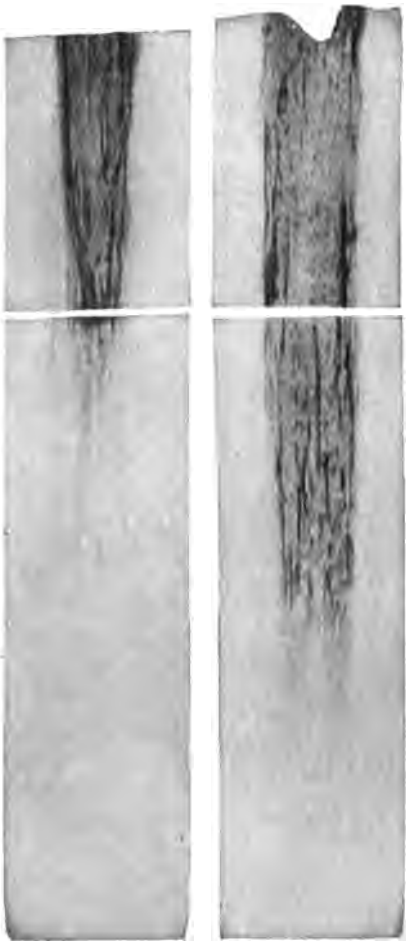


FIG. 144.—Wedge formation of the inner zone in boiler plate.

TABLE XXII

Samples taken	Phosphorus, per cent	Sulfur, per cent
By planing over the whole cross-section at "*a*" (Fig. 96), *i.e.*, only from the outer zone.....	0.048	0.033
Planing over the section to include both outer and inner zones.....	0.085	Not determined
From the inner zone, *K*.....	0.110	0.101

To avoid mistakes of this sort in sampling iron or steel plates, not only for chemical but for metallographic work, the planings or section should be taken, not at the edges of the plate *a-a* or *b-b* in Fig. 145 but at *c-c* or *d-d*.

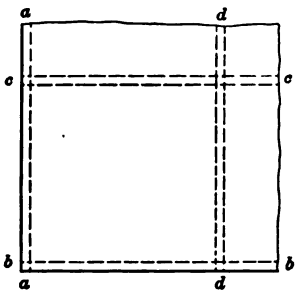


FIG. 145.

Wrought Iron.—The same general rules for getting average samples from wrought iron hold, as in the case of ingots and steel. Whenever it is possible, the shavings should be made by planing over the whole cross-section. As wrought iron always contains slag which is often present in considerable quantities, special care must be taken in collecting the sample as it comes from the planer, because of the fact that the siliceous slag is reduced to a fine powder on planing, and its loss would seriously affect the analytical results. The powdery part is high in oxidic compounds, also rich in phosphorus and silicon. For results which really represent the composition of the sample, it is necessary to weigh the shavings and the powder separately and combine them, in the ratio in which they occur in the original sample, in the preparation of the small sample for analysis. When a wrought-iron boiler plate, for example, was sampled, 42 g. of shavings and 1.3 g. of powder were obtained. Silicon and phosphorus determinations gave the values:

TABLE XXIII

	In the coarse part	In the powder
Silicon	0.06	0.30
Phosphorus	0.23	0.37

It is evident, then, that in order to get a representative sample for analysis, it would be necessary to have the shavings and powder present in the small analytical sample in the ratio of 42:1.3, or about 32 times as much metal as powder.

In the case of puddled iron, the differences are due chiefly to the

irregular distribution of the slag and the presence, therefore, of phosphorus-, silicon- and oxygen-rich spots in the product.

Figure 146 is the cross-section of a link of puddled iron. The very dark spots in different parts of the field indicate local areas rich in phosphorus. Analysis gave:

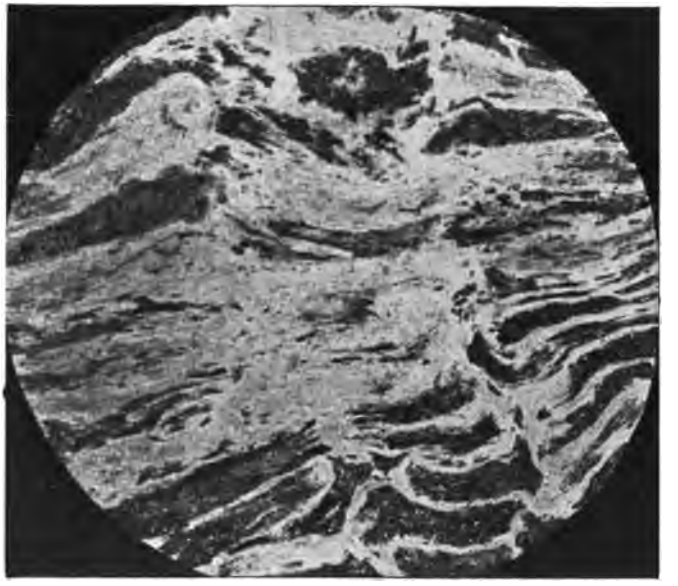


FIG. 146.—Puddled iron.

TABLE XXIV

Samples taken	Phosphorus, per cent
By planing over the cross-section	0.17
By boring in the dark spots	0.30

In a boiler plate, planing over the section showed 0.18 per cent phosphorus, while borings from the dark spots gave 0.29 per cent.

Figures 147 and 148 show etched specimens of wrought iron. The fairly uniform distribution of the dark areas over the entire surface in Fig. 147 indicates a high average phosphorus content. Analysis gave 0.25 per cent.

FIG. 147.

FIG. 148.

Figure 148 shows that in this case the areas rich in phosphorus are local. The values found were:

TABLE XXV

Sample taken	Phosphorus, per cent
By planing over the whole cross-section	0.07
By boring in the dark streaks	0.16

These illustrations show that, in the same specimen of wrought iron, great differences of composition may occur in different parts of the cross-section and of the longitudinal section. In contrast to ingot iron, where the segregation is confined as a rule to definite, and sharply-marked zones, in wrought iron segregated areas are irregularly distributed over the whole surface of the section.

To obtain even an approximately representative sample of wrought iron it is necessary, therefore, to take samples by planing over the entire surface of various parts of the piece and to unite the various shavings. The necessity of collecting the fine powder has been emphasized already.

In wrought iron, the third significant figure is valueless in the percentage found by analysis (even for phosphorus and sulfur) because of the variations in the composition of the original material.

Sampling of Cast and Pig Iron.—*White Iron.*—Perfect sampling of white iron is practically impossible, because it is usually too hard to plane and drilling is difficult and unsatisfactory. Small castings may be broken to pieces, then crushed and in this way a representative sample made; but in most cases, it is a question of sampling a casting so large that it cannot be so treated, and the sampler must knock off small pieces from the large casting. Owing to the abnormal conditions considered on p. 402 the different pieces of a casting may differ considerably in chemical composition. Therefore in a report on an analysis of this sort the chemist should always give the method of sampling and, in case of doubt, should state specifically that the analysis may not absolutely represent the composition of the casting submitted for analysis.

Sampling Gray Iron.—One of the most difficult problems of the steel chemist is to get representative samples of gray iron. The graphite plates distributed through the material make it necessary to use special care in the preparation of the sample for analysis if it is to be at all reliable.

In this case as in all others where a cutting tool can be used, the whole cross-section[1] should be planed down to get an average sample for analysis. Borings should not be used.

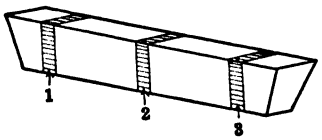


FIG. 149.

During the planing and collecting of the sample, great care must be taken or there is likely to be a large loss of graphite.

For the analysis of a single piece, a pig for example, approximately equal quantities of shavings should be taken from different places (marked 1, 2 and 3 in Fig. 149) and then combined to make an average sample.

Shavings from dark gray iron are never of equal size. On planing, a coarse part I and a finer part II are always formed. The finer part II also contains the graphite plates torn out by the plane. If the shavings are shaken for a long time in a glass bottle, it is usually possible to separate a still finer part which is much richer in carbon than either of the other two. After the sample bottles have been filled with the shavings and allowed to stand for some time, the three grades of material separate of their own accord. The coarsest shavings stay at the top, the next coarser are below in the bottle, and at the bottom are found the finest particles which are rich in graphite.

Even if the contents of the bottle are thoroughly mixed, it is difficult to get a correct average sample for analysis. For exact work, as in an umpire analysis, it is always necessary in this case to divide the sample by sifting it into two or three portions, each part to have material of the same size. The weight of each portion is then taken and, the final sample for analysis is prepared by mixing together some of each sample in the proper proportion by weight. The method is best shown by the following example.

The total weight of shavings made by the plane was 693 g.

[1] Exceptions to this rule will be mentioned later.

By means of sieves this material was subdivided into parts I, II and III

I coarse part = α grams (469 g.)
II middle size = β grams (193 g.)
III finest part = γ grams (31 g.)

To get a 1-g. sample the weighing should be as follows:

$$\text{Of I} = \frac{\alpha}{\alpha + \beta + \gamma} = 0.6768 \text{ g.}$$

$$\text{Of II} = \frac{\beta}{\alpha + \beta + \gamma} = 0.2785 \text{ g.}$$

$$\text{Of III} = \frac{\gamma}{\alpha + \beta + \gamma} = 0.0447 \text{ g.}$$

The three parts should then be combined to make a single sample.

The brass sieve shown in Fig. 150 is well adapted for this use. The upper cover must fit tightly in order to avoid any possible loss of the finest part as dust. Sieves with 80 and 120 meshes to the linear inch suffice for all analytical work.

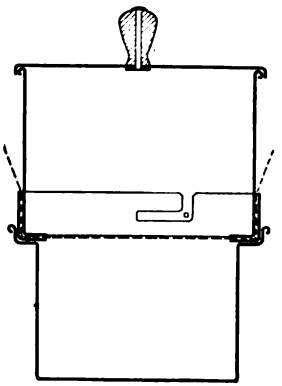


FIG. 150.—Section of brass sieve.

How different the chemical composition of the different parts can be, especially in the percentage of total carbon and graphite, is shown by the following examples.

Example 1.— From a square bar (130 by 130 mm.) of dark gray cast iron, 189 g. were taken by planing over the entire cross-section.

After sifting through an 80-mesh sieve there were obtained:

173 g. of coarse I
16 g. of fine II[1]

[1] Part II showed a distinct tendency to separate on shaking. The shiny black graphite plates collected on the surface and were readily distinguished from the gray iron. A second, finer sieve ought to have been used in this case because the separate graphite determinations varied from 12.64 to 10.68, a deviation which could only be due to segregation.

The analyses are given in the following table:

TABLE XXVI.—DARK GRAY CAST IRON

	I In coarse part, per cent	II In fine part, per cent	Average composition[1] of sample as calculated from I and II, per cent
Total carbon	2.62	11.66	3.39
Graphite	2.38	10.91	3.10
Combined carbon	0.24	0.75	0.29
Silicon	2.44	2.27	2.42
Phosphorus	0.51	0.56	0.515
Sulfur	0.08	0.073	0.079

Example 2.—The differences are even more clearly shown in this second case in which three parts were separated. Planing over the cross-section of a pig of Swedish gray iron gave 696 g. of shavings. After passing through an 80- and a 120-mesh sieve there were obtained:

I = 469 g. coarse particles
II = 193 g. medium particles
III = 31 g. fine particles

Analysis of the three parts gave:

TABLE XXVII.—DARK GRAY IRON

	I In coarse part, per cent	II In medium part, per cent	III In fine part, per cent	Average composition of the pig as calculated from I, II and III, per cent
Total carbon	3.53	4.04	22.00	4.50
Graphite	2.12	2.53	20.94	3.07
Combined carbon	1.41	1.51	1.06	1.43
Silicon	0.81	0.83	0.76	0.80
Phosphorus	0.051	0.044	0.03	0.048
Sulfur	0.017	0.014	0.013	0.016

[1] The method of calculation is:

$$\frac{aI + bII}{I + II}$$

where a is the per cent found in part I and b the per cent found in part II.

For the calculation, then, of total carbon in the table,

$$\frac{2.62 \times 173 + 11.66 \times 16}{189} = 3.39 \text{ per cent.}$$

The differences in the graphite and total carbon content are considerably greater in this case than in the former one.

Finally the total carbon and graphite were determined in a 1-g. sample (taken with reference to the weight of the separate parts as explained on p. 60). The values found were:

Total carbon	4.43 per cent
Graphite	3.03 per cent
Calculated combined carbon	1.40 per cent

These values agree well with the results calculated in Table XXVI. These studies show that in working with iron which is rich in graphite, the analyst must take every possible precaution not only in taking the sample but also in the final weighing; otherwise incorrect results are likely to be obtained.

Inequalities in the Chemical Composition of Gray Iron.—If the shavings to be used for the average analysis are taken from a single place instead of from the whole cross-section, the inequalities in the composition of the casting have an effect upon results obtained by analysis. Sampling by boring is also unsatisfactory if an accurate average analysis is to be made, for with heterogeneous material the sample can be affected materially by the depth of the boring. The following example shows that very considerable differences in composition may exist between different points on the cross-section.

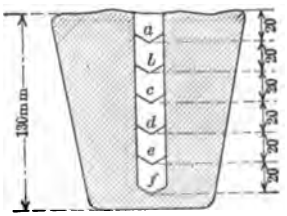


FIG. 151.

Borings were taken from a pig of basic Bessemer iron at points 20 mm. apart as shown in Fig. 151. Determinations of manganese and phosphorus in the borings gave the values shown in Table XXVIII.[1]

The percentage of manganese and of phosphorus is different at each point on the surface of the pig.

Three pigs I, II and III were taken, the first from one end of the bed, the second from the middle and the third from the other end of the bed. Three samples were taken from each pig, at the points marked *O*, *M* and *U* in Fig. 152.

[1] From C. Reinhardt, *Repertorium d. anal. Chem.*, **49**, 744.

TABLE XXVIII

Sample taken at	Manganese	Phosphorus
a	3.42	2.91
b	3.11	2.41
c	3.22	2.65
d	3.11	2.58
e	3.06	2.39
f	3.17	2.65

Tabary[1] found the percentages of total carbon as follows:

TABLE XXIX

Borings taken at	Total carbon in pig		
	I Per cent	II Per cent	III Per cent
O—top	3.53	3.55	3.44
M—center	3.55	3.72	3.55
U—bottom	3.01	3.44	3.40

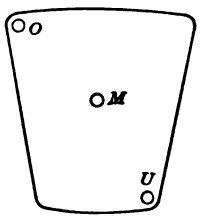


FIG. 152.

The percentage of carbon is greatest in the center and least at the bottom of the pig.

Sampling in Special Cases.—In addition to the unintentional irregularities in the composition of a sample of steel or iron, which are due to segregation, decarbonization, excrescences on cast-iron and the like, local changes are sometimes produced intentionally during the process of manufacture. The commonest illustration of this sort of local change is that produced by the operation of case-hardening where the outer layer becomes much richer in carbon than the soft steel core. In a case of this kind, an average analysis, for which samples are obtained by planing over the entire cross-section, is of little value. The important question is to determine how much carbon has been taken up and the

[1] P. TABARY, *Stahl u. Eisen*, **1894**, 1075.

depth of the carbon-rich zone. In this case the metallographic examination should always precede the chemical analysis. (See p. 395.)

Frequently the piece is quenched from red heat after its exposure to the case-hardening material. The outer layer, rich in carbon, becomes hard while the inner core remains soft. If such a hardened piece is to be analyzed, it must be annealed in order to make it possible to take the sample. Special care must be taken during the annealing not to lose carbon by superficial oxidation. The precautions to be taken have been described on p. 425. Care must be taken, also, to avoid a transfer of carbon from the richer outer layer to the interior. The annealing time, therefore, is made as short as possible (about ¼ hr.) and the annealing temperature is also kept as low as possible (750 to 800°C.). If the specimen in question is ordinary carbon steel (not a special steel), it may be quenched in water after the furnace temperature has fallen below 700°C. since hardening does not take place below the pearlite point. If these precautions are taken during the annealing, the transfer of carbon is very slight.

Magnetic Testing and X-ray Examination of Steel.—A discussion of the methods of testing steel would not be complete without a brief reference to two modern aids to the metal inspector, the magnetic testing device and the x-ray study of metals for the purpose of detecting blow holes, slag inclosures and similar defective areas. Neither method is fully developed at the present time but in certain cases the methods will give results of the greatest practical value which can be obtained in no other way. Both methods have the added advantage that each may be used without injuring in any way the material under examination.

The possibility of making use of the magnetic properties of metals as a means of determining their mechanical properties has been a subject of discussion and careful experiment for many years. Investigation of the problem, as it is applied to the detection of heterogeneous material, has been carried out for a number of years under the direction of Dr. Charles W. Burrows of the magnetic section of the Bureau of Standards. Mr. Frank P. Fahy of the Pennsylvania Railroad had also been investi-

gating the problem, and in 1911 the two investigations were combined and have continued since that time. Through the efforts of these men and with the active coöperation of other investigators many of the practical difficulties have been overcome and instruments have been devised which make the method of magnetic testing of very great value in special cases.[1]

The main problem of magnetic analysis is the correlation of the magnetic and mechanical properties of steel.[2] Various magnetic characteristics have been studied in this connection, but the one most commonly used is permeability, the ratio between magnetic induction and the magnetizing force. For the determination of permeability Fahy[3] has devised an extremely sensitive permeameter.

Two phases of magnetic testing have to be considered, first, a study of the average character of the specimen under examination, whether it has been quenched, annealed, strained or otherwise altered; and second, whether a specimen of some length, like a steel rail, is uniform throughout or whether it contains defects like blow holes, slag spots and the like. Both of these needs have been combined in Burrows' instrument, the Magnetic Analyzer, which is so arranged that the magnetic condition of the material under test can be observed on a translucent scale or it can be recorded photographically. The general nature of the curves obtained is shown in Fig. 153. The most important problem which has been undertaken, up to the present time, is the study of steel rails and the results have been so satisfactory that the method has been adopted as a standard control method on one of the large railroads. It is not improbable that the method may be so modified as to make it possible to study rails in actual service, permitting their removal before complete fracture occurs.

Magnetic analysis has also been applied with success to the testing of steel wire, strips or cable which can be pulled through

[1] A discussion of Magnetic Analysis is given in the *Proceedings of the American Society for Testing Materials*, **19**, (1919) Part II, from which is taken most of the information given here on magnetic testing. A description of the instruments used is given in detail in *Bull.* 41 of Holtz and Company, New York.

[2] "Correlation of the Magnetic and Mechanical Properties of Steel," *Scientific Paper*, **272**, U. S. Bureau of Standards.

[3] *Chem. and Met. Eng.*, **19**, 339 (1918).

the solenoid coil of the instrument at a fairly high rate of speed. Marked irregularities in the magnetic curve indicate inequalities or more serious defects in the material under test.

X-ray Examination of Defective Metal.—The metal specimen to be examined is placed in contact with an x-ray plate, and both are protected against interfering rays by means of a suitably arranged lead screen. An exposure is then made using a Coolidge

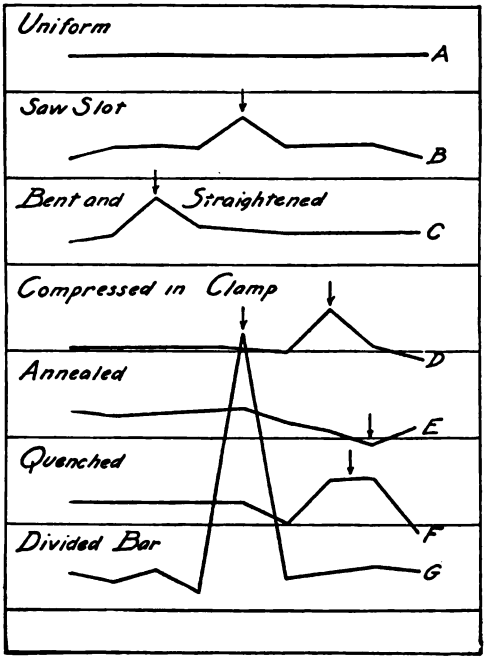


FIG. 153.—Magnetic permeability curves.

tube as the source of rays, the length of exposure depending on the nature of the material, the thickness of the metal, and the voltage of the current used to produce the rays.

The method has been used chiefly in the study of autogeneous welds and castings suspected to contain blow holes, Fig. 154. Up to the present time it has been applied only to steel specimens less than 1½ in. thick. The radiograph shows only the massive structure of the metal, and gives no information as to grain size

or crystal structure. It does, however, give valuable information as to the presence of blow-holes, slag inclusions, porous spots and similar defects, and has the distinct advantage that the

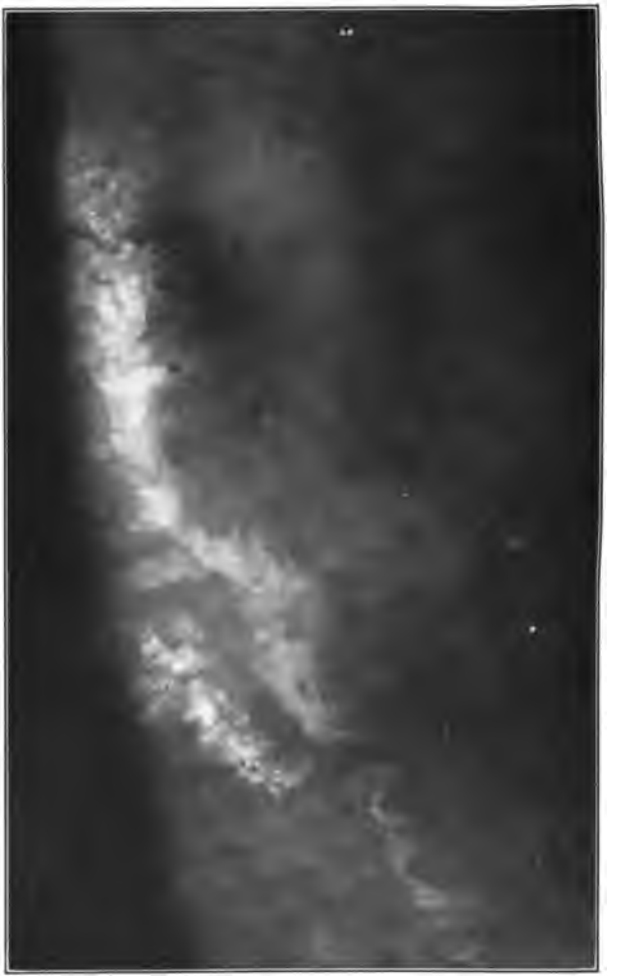


FIG. 154.—*X*-ray photograph showing blow holes in steel. (*Davey.*)

test does not involve the cutting or drilling of the material. No fluoroscopic screen which is sensitive enough to make possible the visual examination of metals has yet been developed so that,

at the present time, work with metals must be done by means of x-ray photographs.

The method is expensive, and its applications are limited as yet, but in those cases in which it has been used the results are of great value.[1]

[1] Information concerning metal radiography was obtained from Dr. W. P. Davey of the General Electric Company by whom the radiograph Fig. 154 was taken.

CHAPTER XXIX

THE ALLOYS OF COPPER

The alloys of copper, which include the brasses, bronzes, heavy bearing-metals and the like, are next in importance from an industrial standpoint to iron and steel and with them, too, the microscope is an almost indispensible tool for the metal tester. Metallographic examination of these alloys is not so important as it is in the case of iron and steel from the view point of the analyst who is interested in getting representative samples, as segregation is so much less strongly marked. The physical properties of the copper alloys change so rapidly, however, when they are subjected to mechanical work, that in many cases the chemical analysis alone will give no information at all as to the value of the material for a given purpose. In a few cases segregation does take place to a marked degree, and sampling without an examination of the specimen is of no value.

Preparation of the Specimens.—Several conditions, which will be considered in detail later, are involved in the study of metals which have been worked, and each case may need a sample of a different kind. There are many articles made from brass, for example, which are subjected to severe strain at but one point, or at least within a very limited area. In such cases it is necessary to take only a small section from the danger point, to determine whether or not the material is safe to use. On the other hand, it may be very necessary to know whether or not the material is homogeneous throughout a considerable length, or over a large area. In such a case a large specimen, or a number of small specimens at different points, must be taken. This lack of homogenity is illustrated in Fig. 155, which shows the wide variation in appearance of a brass shell-case over a comparatively limited area. The differences in the physical properties at the different points are very marked. As the specimen shown is perfectly homogeneous chemically, the value of microscopic examination is obvious. It also illustrates the

necessity of a careful selection of the metallographic sample, when it is known that the material has been subjected to unequal amounts of work in its fabrication. The selection of the sample, then, is one which cannot be made wholly at random, but which

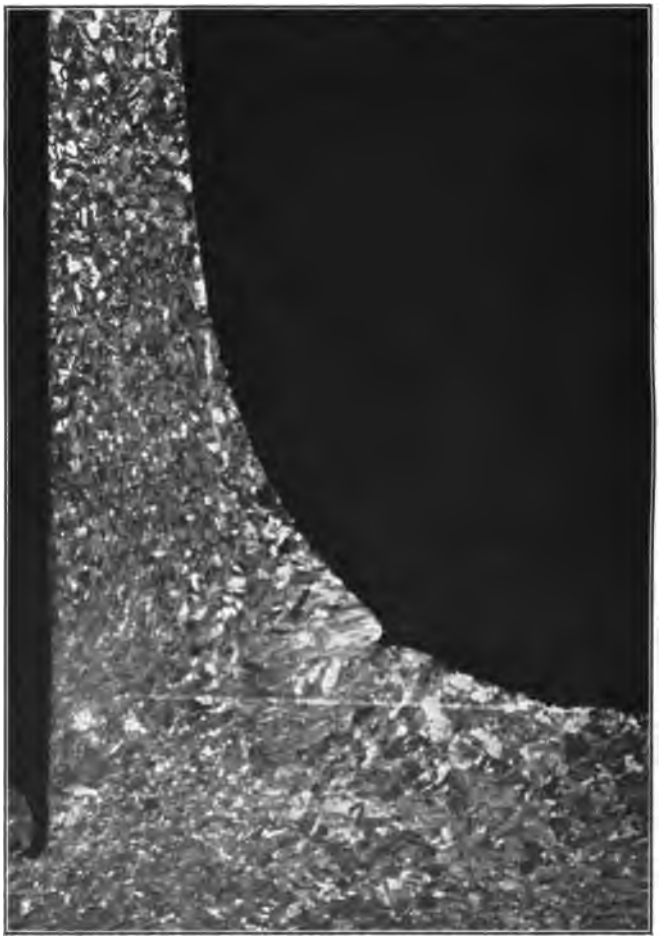


FIG. 155.—Section of brass shell case. 10 ×.

requires thought on the part of the sampler, if the specimen examined is to give a true indication of the character of the metal of which it is a part.

Polishing.—After a specimen of suitable shape and size has been selected for examination, the piece is filed and polished in the way indicated in discussing the preparation of iron and steel specimens (p. 338), except that in this case, the grinding and polishing operation can usually be carried out with a smaller number of abrasive papers. For common brass and bronze pieces, the following sequence of abrasives will do the work. Coarse file, fine file, French emery paper (Marke Hubert) 1C, 0, 00, 30-min. emery in suspension, and alumina or rouge in suspension, the two last abrasives being used on rotating disks. It is seldom necessary to use emery paper finer than 00, except with very soft alloys rich in lead (the plastic bronzes) with which 000 or even 0000 emery paper is needed to get a satisfactory surface. If these fine papers are used, they should be kept moist with light machine oil during the polishing operation. The copper alloys are scratched so much more easily than steel or iron that they must be held very lightly against the rotating disks used in the final polishing operation. It is hardly necessary to say that even greater care must be taken with these relatively soft specimens **to avoid the transfer of coarse abrasive to a surface on which a finer powder is to be used.**

Etching of Brass and Bronze.—Numerous etching reagents have been used for these alloys, the selection depending to a large extent on the way in which the specimen is to be used.

1. *Nitric Acid.*—Nitric acid, d. 1.2, is a useful reagent for the rapid examination of the specimen at low magnifications (100 diameters or less). It develops the crystalline structure readily, with strong contrasts between crystals of different shapes and sizes. It is especially useful in the macroscopic study of large specimens which, because of their size, cannot be polished as perfectly as the small pieces commonly used. The chief objection to the use of nitric acid is that it has a tendency to attack the crystal boundaries so strongly that details of the structure are wholly lost. Consequently it is of little use for specimens which are to be examined and photographed at magnifications of 200x[1] or greater. Nitric acid is used either by application to the specimen with a swab held in forceps, or by immersion of the specimen. The latter method is rather easier to control, but in

[1] The symbol 200x is used to indicate a magnification of 200 diameters.

this case the specimen must be agitated constantly during its immersion in the acid, or the gas bubbles must be removed by means of a brush. Otherwise uneven attack will cause an appearance of the specimen which is quite misleading. Where photographs are to be taken at 5 or 10 diameters this acid is probably the best reagent.

2. *Ammonium persulfate*, $(NH_4)_2S_2O_8$, in strong ammonia (1 g. in 20 c.c. NH_4OH d. 0.90) is often used to identify β-brass (p. 454), which it attacks readily, leaving α-brass (p. 454) practically unattacked.

3. *Ferric Chloride solution*, made by dissolving 10 g. of ferric chloride crystals in 100 c.c. of alcohol, is an excellent reagent for the etching of arsenical brass.

4. *Alkaline Hydrogen Peroxide.*—The most effective reagent for ordinary brass, and for most copper alloys, is a solution of hydrogen peroxide (H_2O_2) made alkaline with ammonium hydroxide. The ratio of peroxide to ammonium hydroxide is determined by the composition of the alloy under investigation, but for most purposes one of the following compositions will be found satisfactory:

Zinc less than 10 per cent, 1 c.c., peroxide to 2 c.c., ammonium hydroxide.
Zinc from 10 to 30 per cent, 1 c.c., peroxide to 5 c.c., ammonium hydroxide.
Zinc from 30 to 40 per cent, 1 c.c., peroxide to 10 c.c., ammonium hydroxide.

(These proportions are only suggestive for the concentration of the peroxide solution changes rapidly on standing and the best proportion should be determined by trial.)

It is of the greatest importance, in the application of this solution that it should be made from fresh and strong reagents, immediately before use. The chief cause for failure is in the use of material which has been allowed to stand. The method of using alkaline peroxide is as follows. Hold the specimen to be etched under running water until the surface is thoroughly wet, then apply the reagent by means of a swab of soft cotton and rub the surface vigorously for a few seconds. Hold the specimen under the tap until the reagent has been removed, and again apply the peroxide. Repeat these operations, of rubbing with the etching reagent and flushing with water, until the desired amount of etching has been done. If the operation has been

carried on successfully with suitable reagent, the surface of the brass or bronze should show a perfect development of the crystalline structure of the metal, and details of the crystal formation should be clearly marked. The operation of etching should not take more than 5 min. Dark, over-etched surfaces, where the detail of the structure is obscured by thick boundary lines between crystals and frequently by black irregular patches over the entire surface of the specimen, are usually due to an excess of ammonium hydroxide. The surface may be cleared and the true structure developed, in a case of this kind, by using a fresh mixture of reagents in which the peroxide is present in a slightly greater quantity than would normally be used. Light colored surfaces, in which little or no detail of the structure is visible, are usually due to an excess of peroxide in the etching liquid. The difficulty may be overcome by the addition of strong ammonium hydroxide to the reagent. In a few cases, however, the lack of detail in the structure is due to overstrained metal. Brass or bronze may be so severely overstrained by mechanical work that the development of a definite crystal structure is very difficult. In most cases of this kind, it will be possible to recognize the crushed cyrstal masses at some part of the surface under inspection, so that the reason for the lack of development will be evident.

Alkaline hydrogen peroxide reacts differently from the persulfate mixture; with the former the α-brass (p. 453) is colored yellow or brown and β-brass (p. 454) is almost unaffected, while with the persulfate, β-brass is the constituent attacked.

Copper and Its Alloys.—In addition to pure copper, which is often submitted to the chemist for examination, the alloys most commonly encountered are those of copper with zinc (the brasses) and those of copper with tin (the bronzes). Many possible alloys may be made of the bronze type or of the brass type, but the detection of slight differences of composition is a problem for the chemist, not for the metallographer. Zinc, in small amounts, is often added to tin-bronze to make the molten metal more fluid for casting purposes. Conversely one or more per cent of tin is often added to certain of the copper-zinc alloys to make them more resistant to corrosion. Arsenic, antimony, bismuth, iron and other elements in small quantity are often

found in brass or bronze, because of impurities in the ores from which the alloying metals were originally made. These elements, whether added intentionally or present as impurities, are of very real importance to the metal tester, but can be determined at present only by accurate chemical analysis. In brass and bronze lead is the only common foreign element whose presence can be readily detected by the microscope. It is frequently added to these alloys with the idea of improving the machining qualities of the metal, and is visible under the microscope in the form of more or less circular spots, the cross-sections of the drops in which the lead is present in the alloy. Lead is more readily seen in the unetched specimen, and the microscope tells whether it is uniformly distributed throughout the metal mass in which it occurs. Figure 156 shows the fairly regular distribution of lead drops through a sample of bronze, and Fig. 157 is a bearing metal in which marked irregularities in the distribution of the lead are evident. Plastic bronze, which is made by cooling an emulsion of molten lead and molten copper, two elements which do not mix even in the liquid condition, often contains 50 per cent of

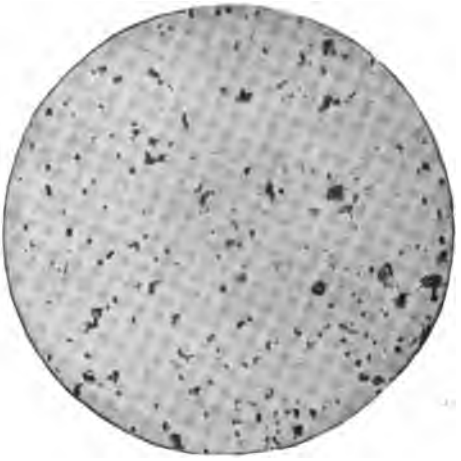


FIG. 156.—Unetched bronze showing lead drops. 75 ×.

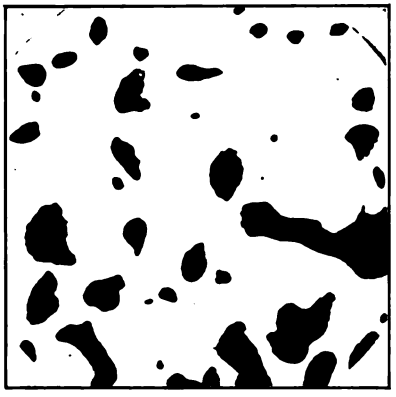


FIG. 157.—Irregular distribution of lead in defective plastic bronze. 75 ×. (*Homerberg.*)

lead. If it is to be of service in heavy bearings this lead should be distributed as uniformly as possible throughout the copper matrix. The microscope gives the best possible means of determining whether or not the plastic bronze was correctly made.

The chief uses of the microscope in connection with the brasses and bronzes are these: (1) To determine whether the metals of which the alloy was made have been uniformly mixed, a question which is of great importance in dealing with those alloys which have a duplex structure. (2) To determine the character,

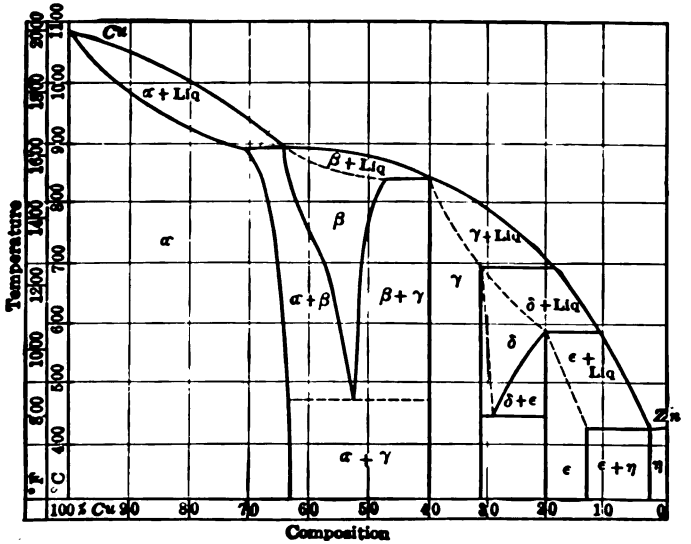


FIG. 158.—Copper-zinc diagram. (*Shepard.*)

amount and distribution of the non-metallic impurities (p. 456). (3) To determine the amount and nature of the work done on the alloy, and to study the effects which may have been produced by annealing. This last function of the microscope in the testing of copper and its alloys is by far the most important as it makes it possible to find in the properties of the metal differences of which the chemical analysis would not give the slightest suggestion.

To come back to the question of uniform mixing of the alloy, it is evident that one of the best indications of lack of uniformity is to find microscopic evidence of a duplex structure when but one crystal form should be found, or conversely, to find but a single

crystal form in a given area when two forms ought to be present. The metal tester must know, then, whether a single crystal type or a duplex structure is to be expected. This information is most easily found by reference to the equilibrium diagrams, Figs. 158 and 159. These diagrams are read in the same way as the steel diagram, p. 356, and give to the metal tester the needed information as to the general character of the alloy

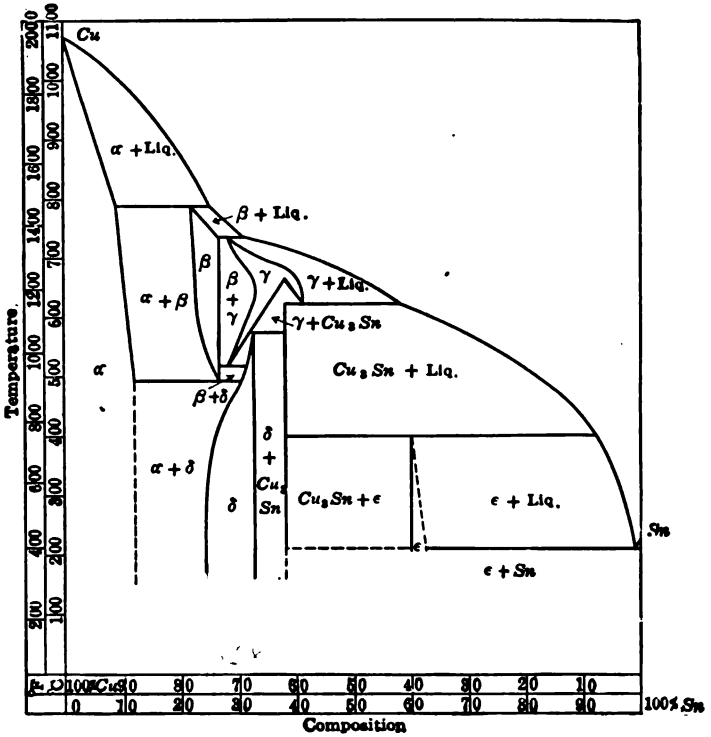


FIG. 159.—Copper-tin diagram.

under inspection. The application of these diagrams to concrete cases may be illustrated by a few examples. In Fig. 158, which refers to the alloys of copper and zinc, it will be seen that an alloy containing 30 per cent of zinc (or any other alloy containing less than about 35 per cent of zinc) will be found in that section of the diagram marked α and ought, therefore, to be a perfectly homogeneous solid solution, and should show but one kind of crystal

under the microscope. Cast brass usually cools off too quickly to allow time for the formation of perfectly uniform crystals so that it commonly has the appearance shown in Fig. 160 in which the dark worm-like masses are parts of the crystal slightly richer in copper than the major portion of the mass. Very slow cooling from the molten condition or annealing of the solid mass will cause a diffusion of the copper in the solid metal with the formation of the uniform crystal shown in Fig. 161. The copper-zinc alloys in this range (from about 5 to approximately 35 per cent zinc), usually known as the α-brasses from their relation to the diagram, are the most important of the brass alloys. The α-brass, containing 30 per cent of zinc, often called 70-30 brass, is perhaps the most important of all the copper alloys. The succeeding areas on the diagram are not so sharply defined as the α-section, but under normal conditions α- and β-brass may be expected in the range between 64 and 58 per cent copper, with pure β-brass in the range between 58 and 50 per cent of copper. The diagram indicates another fact of importance to the metal tester who is interested in the history of the metal under examination, namely that all alloys beyond the α-range are composed of

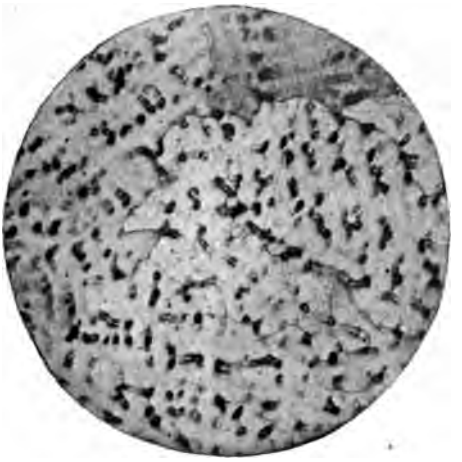


FIG. 160.—Cast α-brass. 75 ×.

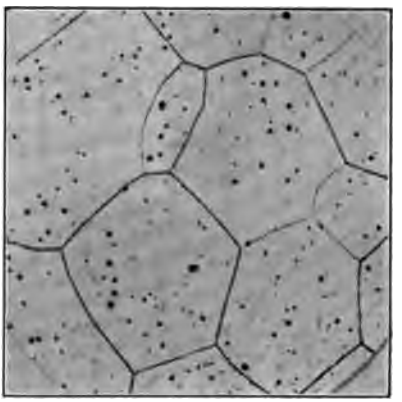


FIG. 161.—Solid solution of zinc in copper. (Dark spots are lead.) 75 ×. (*Homerberg.*)

two elements α and β, or α and γ if the melted metal is slowly cooled. It also shows that homogeneous β-brass is found only in the triangular area above 460°C., between approximately 50 and 60 per cent of copper. The microscope would show but one kind of crystal if the alloy was examined at the higher temperature or, which is the usual case, if the alloy had been quenched from some temperature above that at which pure β-brass ceases to exist. Figure 162 shows a section of Muntz metal (copper 60 per cent, zinc 40 per cent) which has been cooled quickly from 750°C., and should, in accordance with the diagram, be homogeneous. This specimen appears to be fairly homogeneous. The small amount of a second type of crystal indicated by the dark dots is due to the fact that the cooling was not fast enough to overcome wholly the tendency for the alloy to separate into its two compononents, as it would have done on slow cooling, as is shown in Fig. 163, an alloy of identical composition cast in the ordinary way and allowed to

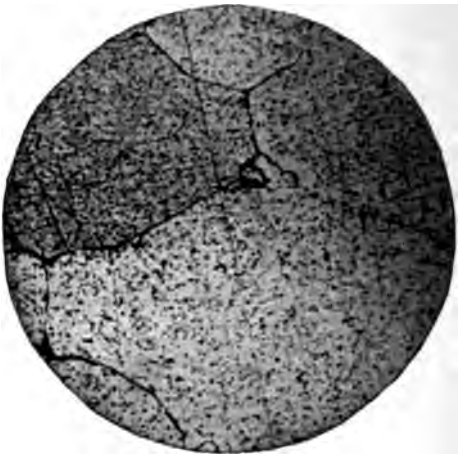


FIG. 162.—Muntz metal annealed at 750° and quenched. Chiefly β-brass. 75 ×. (*Johnson and Jermain.*)

FIG. 163.—Cast Muntz metal. 150 ×.

These illustrations from the α- and the β-brass sections of the diagram serve to illustrate the way in which the diagram may be applied in technical work and also, the sort of information that the microscope will give that cannot be obtained by chemical methods.

Fortunately for the metallographer and the metal tester, the copper-zinc alloys in which the percentage of zinc is greater than 50 are so brittle that they are never used for purposes in which the strength of the material is a factor, so that for practical purposes the α- and β-forms are the only ones which need be studied.

The bronze diagram (copper-tin) is even more complex than that of the copper-zinc alloys, but in this case, too, the alloys containing more than 25 per cent of tin are too brittle for industrial purposes, except in the making of decorative castings. Therefore, as the diagram indicates, the inspector has to deal only with the α- and β-forms, as with the zinc alloys. In this case, too, the diagram indicates that homogeneous β-bronze exists only in a very limited area, in the temperature range between about 500 and 800°C., and when the composition is from 75 to 80 per cent copper. Again the microscope is of service, for the detection of an homogeneous specimen of bronze of this composition would indicate positively that the metal had been quenched from the higher temperature.

When bronze is cast from the molten state, it hardens so much more rapidly than ordinary brass that there is not time enough for as complete an equalizing of the composition of the α-crystals. The result is that the etched section of the bronzes, whether ordinary tin bronze, or phosphor or silicon bronze, commonly shows the characteristic dendritic structure illustrated Fig. 164.

The second important application of the microscope to the copper alloys is in the study of the non-metallic inclusions, which are sometimes present and are so difficult to detect by chemical methods. Copper and its alloys which have been "burned," or from which the oxygen has not been sufficiently removed by phosphorus, magnesium, boron or other deoxidizing agent in the process of manufacture, contain varying amounts of copper oxide, which forms a eutectic mixture with copper and may have an extremely harmful effect on the properties of

the metal. The oxide has no strength or ductility, and is a real source of weakness if it is present in any appreciable am It is especially harmful if the copper or bronze is to be mad

FIG. 164.—Dendritic structure of cast phosphor bronze. 75 ×.

electrical apparatus, as the presence of even a minute am of the oxide will cause a sharp decrease in the conductiv

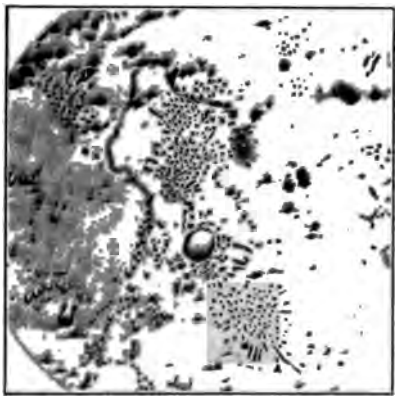


FIG. 165. Copper oxide eutectic in copper. 100 ×. (*Fay.*)

FIG. 166.—Slag areas in d brass tube. 75 ×.

the metal. The appearance of the copper oxide eutectic is found in bad cases is shown in Fig. 165 and of inclosed s Fig. 166.

Other non-metallic impurities, which occur much less frequently in non-ferrous alloys than in iron and steel, have been described.[1]

The Study of Worked Material.—The third, and far the most important application of the microscope to the study of the brasses and bronzes, is in the examination of material which has been subjected to mechanical work, rolling, drawing, hammering or the like and, as a corollary to this, in the study of metal which has been annealed after the cold work has been done.

If a metal is subjected to a moderate amount of cold work, such that its elastic limit is not exceeded, no change in its structure will be noticed under the microscope, but a very slight increase above the elastic limit causes a change in the structure which is evident at once. A highly polished specimen which is subjected to tension while it is in position under the microscope, begins to

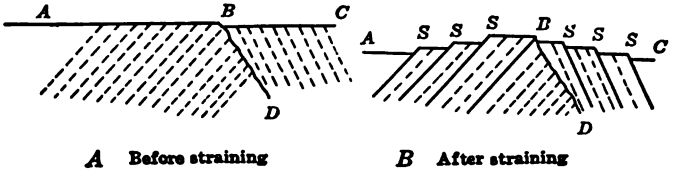


FIG. 167.—Sketch showing the way in which slip bands are produced in strained metal. (*Rosenhain.*)

show a small number of black lines as soon as the elastic limit has been passed. These lines are practically parallel on any one crystal, but their direction varies in adjacent crystals. They do not cross crystal boundaries, and are, therefore, due to a change in the individual crystals rather than in the entire mass of metal. As the amount of strain increases, these parallel lines become more numerous until, at a point just before the material breaks or crushes, the entire surface is covered with a mass of of lines, giving to the material a distinctly fibrous appearance under the microscope. The most commonly accepted theory to account for these changes is that the very small layers, of which the larger crystal grain is composed, actually slip on each other so that the surface of the polished specimen is no longer smooth but corrugated, as indicated in the sketch, Fig.

[1] COMSTOCK, *J. Am. Inst. Metals*, March 1918. CARPENTER and ELAM, *J. Inst. Metals* (British) **19**, 155 (1919).

167, the number of ridges increasing with the amount of strain to which the metal has been subjected. The dark lines are due to the fact that the light coming through the microscope tube is not reflected back into the tube from all parts of the surface, but that part of it is reflected out of the field of vision when it strikes the inclined surfaces of the ridges formed by the slip. Rosenhain has called these dark lines "slip bands," and the term has come into general use.

Another phenomenon, closely allied to the formation of slip bands, is the production of what has been called "amorphous cementing material" along the planes where slipping occurs. The following theory, first proposed by Beilby, is generally, though by no means universally, accepted. The assumption, for which much experimental evidence has been produced, is that when the crystal planes glide or slip on each other, a small amount of material is produced which is amorphous in character and is much harder, tougher but less elastic than the material from which it is formed. As the amount of strain increases the amount of amorphous material also increases, and those properties which are characteristic of the amorphous material become more strongly marked. The practical effect of the formation of this amorphous cementing material is well known, as it is the cause of the hardening of rolled copper sheets, the production of spring brass wire by cold work and other operations of the same sort where mechanical work greatly increases the hardness and tensile strength of the material. The amount of amorphous material which can be produed safely in practice is limited by the fact that brittleness, as well as hardness, accompanies its formation, so that if the metal is to withstand shock the amount of amorphous substances must be carefully controlled.

Neither slip bands nor amorphous material can be seen under the microscope when the specimen is polished in the usual way, but both effects make the specimen readily susceptible to local etching attacks with the formation of characteristic dark lines and bands which are distinctly visible even at low magnifications. These lines or bands which have been developed by the etching of a strained metal are often known as "etch bands," and are of the greatest significance to the metal tester.

The fibrous structure, which is so characteristic of badly over-

strained material, is shown in Fig. 168, a brass tube having the composition 70 per cent Cu and 30 per cent Zn. It is a remarkable fact, and one which should be noted by the metal inspector that a very badly strained specimen, like the one shown in the figure, is much harder to etch than any other type of brass or bronze. Long etching with fairly strong reagents is needed to develop the structure at all, and the contrast between the different parts of the crystal is so slight that satisfactory photographic reproduction is practically impossible. The fact of importance to the metal tester, then, is that a hard, structureless surface, whose fibrous character is shown only by severe etching, always indicates an excessive amount of work which has not been relieved by annealing.

FIG. 168.—α-brass strained and not annealed. 75 ×.

Annealing.—The brittleness produced by cold work is so harmful in most cases that it is necessary to soften the material by the operation of annealing. The work which is done in the shaping of a brass or bronze piece may be unequally distributed over the material, and so may cause brittleness at some points and not at others, leading to a condition of uneven strain which is more dangerous than uniform brittleness. In this

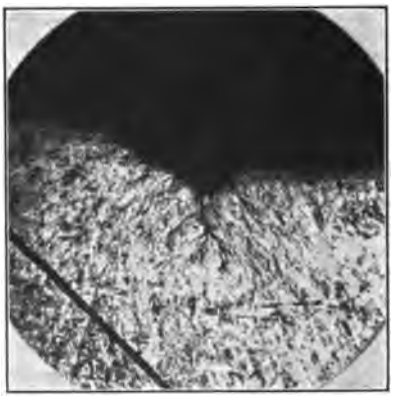


FIG. 169.—Fibrous structure and crack in strained α-brass. 25 ×.

case, annealing is used not merely to decrease the brittleness of the material, but to relieve the uneven strain produced by the cold work. Figures 169 and 170, sections of a brass shell case, illustrate the effect of cold work unevenly applied. The drawing operation was of such a character that a great amount of work was done in a very limited area, leading to a distinctly fibrous structure and, at the point of greatest strain, an actual crack. The effect of annealing following mechanical work is a most striking one, and gives to the metal tester information concerning the heat treatment of the material which can be obtained in no other way. The strained or crushed material begins to recrystallize when a moderate increase in temperature takes place.

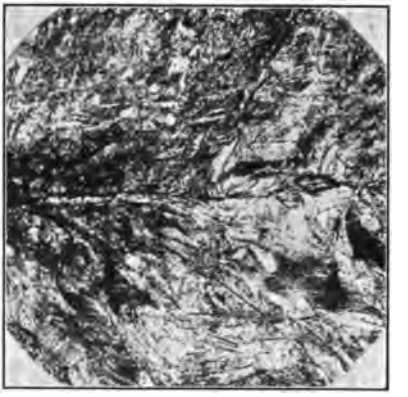


FIG. 170.—Badly strained α-brass. 75 ×.

FIG. 171.—Strained α-brass incompletely annealed. 75 ×.

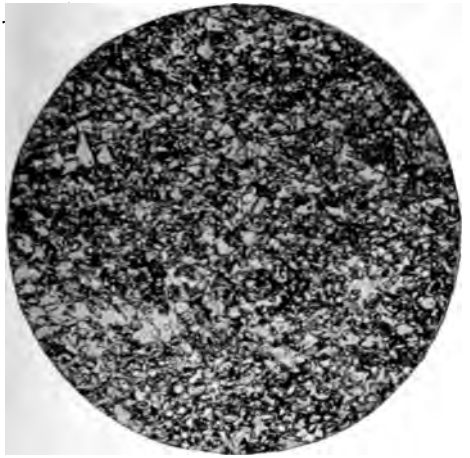
The recrystallization is accompanied by a characteristic "twinning" of the crystals which, after etching, appear under the microscope as alternate light and dark bands crossing the crystal grain but stopping, as do the slip bands, at the grain boundaries. The first step in the recrystallization takes place at a temperature which depends on the amount of work done on the material, and is indicated by the irregular distribution of large and small crystal masses shown in Fig. 171. A structure of this kind, which is formed at what is called the "recrystallization tem-

perature," is distinctly undesirable as it is composed of large masses of the hard, unannealed material in contact with the small twin crystals, and is therefore distinctly heterogeneous. Although the chemical analysis might be good, the metallographer would know at once that the heat treatment had not been satisfactory, and would condemn the material if it were to be used under conditions in which it would be subjected to shock.

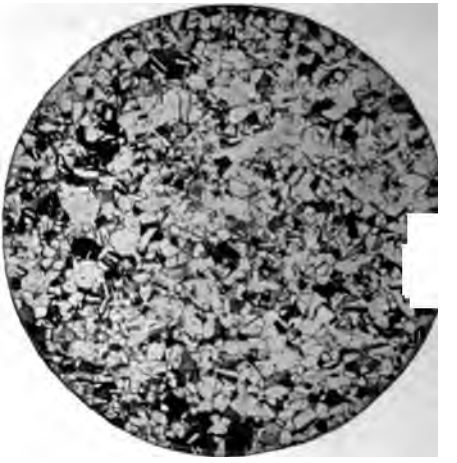
As the annealing temperature increases the twinning becomes more evident, and the size of the crystals increases. It may be said, in general, that the higher the temperature the larger the crystal grains, other conditions being equal; but it is also true that the crystal size depends to an extent on the amount of work done on the material before annealing. Figure 172 shows the appearance of cold-worked and annealed brass under varying conditions of heat treatment. *A* is characteristic of severely worked brass which has been annealed at a temperature slightly above its recrystallizing temperature, and indicates a metal which is hard, springy, strong and not very ductile. *D*, on the other hand, shows a brass which has been annealed at so high a temperature that it is practically "dead soft," with low tensile strength and no springiness whatever. Micrographs *B* and *C* represent intermediate conditions in which either the amount of cold work has been less or the annealing temperature higher, and the resulting metal would have properties intermediate between *A* and *D*.

The question of grain size has come to be of such importance in standardizing materials for engineering purposes that the American Society for Testing Materials has adopted certain conventions that will be of great service in unifying micrographic practice and making results from various sources truly comparable.

Magnifications.—For general use the magnifications shall be 10, 25, 50, 75, 100, 200, 500, and 1,000 diameters.



A. Severely cold worked cartridge metal beginning to recrystallize. 75 ×.



B. Cold worked and annealed. Small twi crystals are visible. 75 ×.

C. Moderately cold worked cartridge metal after annealing. 75 ×. (The characteristic twinned structure is very marked.)

D. Moderately cold worked cartridge bras annealed at 700°C. 75 ×. (Large twin crys tals due to overheating.)

FIG. 172.— Brass 70 per cent copper, 30 per cent zinc.

For Showing Grain Size.—The following magnifications are recommended:

TABLE XXIX

Material	Cast	Wrought
Steel and ferrous materials	100 diameters	100 diameters
Copper	50 and 100 diameters	75 diameters
Copper-zinc alloys	50 and 100 diameters	75 diameters
Lead-tin-antimony alloys	50 and 200 diameters	

Grain Size.—In making grain size measurements, two classes of alloys need to be considered:

1. Alloys consisting of but one type of crystal, as copper, α-brass and the like and

2. Alloys consisting of two or more metallographic constituents like the steels, Muntz metal, p. 454, solder, babbitt metal, p. 474, etc.

If an alloy of the first class happens to show the twinned structure, the original crystal, **including the twinned layers,** is always called one grain. In an alloy of the second class, the original grain which has broken down into the two components is taken as the unit, if it can be determined, or if the decomposition into its components has taken place in such a way as to destroy the outlines of the original crystal, the individual component is taken as the unit of measurement.

Two methods of measuring grain size are in use, depending on the condition of the material under examination. If the material has grains which are equi-axed (axes of the same length), as is the case with most metals which have been cast or fully annealed, a method based on the number of grains included in an area of definite size is generally used. The method recommended by Zay Jeffries[1] (p. 466) is simple and accurate. Whatever method of grain counting is used, the circular area should always include at least 50 grains in order that an average measurement may be obtained.

When a metal has been strained by rolling, hammering, drawing or a similar operation, the grains are no longer equi-axed, but are more or less elongated in the direction in which the

[1] ZAY JEFFRIES, "Grain Size Measurements," *Met. and Chem. Eng.*, **18**, 185.

greatest amount of strain occurred as, for example, in the direction of rolling or drawing. (Figs. 173 and 174.) In such a case

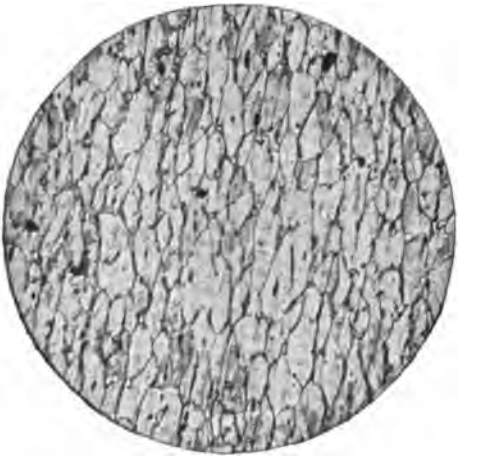


FIG. 173.—Moderately worked Muntz metal (Cu 60 per cent–Zn 40 per cent). 75 ×. (*O'Daly.*)

Heyn's intercept method is used, the average grain size being determined by counting the number of grains at a given magnifi-

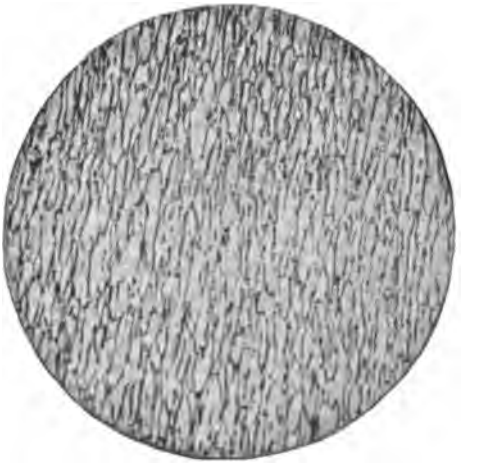


FIG. 174.—Specimen.—After hard drawing.

cation, along lines of known length, on axes perpendicular to each other with one of the two axes parallel to the direction of

drawing or rolling. If the material is apparently composed of very non-uniform crystals, it may be necessary to prepare a new surface, and take a third crystal count along a line at right angles to the other two.

Several methods of expressing the numerical values of the grain size are in use, the commonest and most useful system, in the case of equi-axed grains, is to indicate the number of grains per unit area (square inch or square millimeter). It is not so satisfactory to report the average area of a grain, although this method is sometimes used. The average linear dimensions of the grain may also be used to indicate the grain size. With elongated crystal grains, the grain size is expressed by giving the average number of grains per linear unit in two (or three) directions. The average number of grains per unit area may be given as well as the ratio of length to width of the grain.

Of the various methods of making grain size measurements, the most convenient one is that of Jeffries referred to above. This consists in projecting the magnified image of the specimen onto a ground glass plate on which has been inscribed a circle 79.8 mm. in diameter (area = 5,000 sq. mm.). The ground glass is placed in position in the metallographic camera with its ground surface toward the specimen, and on the outer, smooth surface the number of whole crystals included in the circle is counted. This may be done conveniently by checking each crystal with a soft (glass) pencil. The number of grains intersecting the circumference is then counted, and 0.5 of this number is added to the number completely included in the circle, giving a close approximation to the whole number of crystals present. To obtain the number of grains per square millimeter, the crystal count is multiplied by a factor which depends on the magnification used. These factors are given in Table XXX.

Instead of using a circle, as indicated in Table XXX, it is possible to use a rectangle having the same area (5,000 sq. mm.). The following dimensions will give rectangles of approximately 5,000 sq. mm.:

70.7 by 70.7 mm.
65 by 77.0 mm.
60 by 83.3 mm.
55 by 91.0 mm.

TABLE XXX

Magnification used (m)	Diameter of circle in millimeters	Multiplying factor (f) to obtain grains per square millimeter
Full size	79.8	0.0002
10	79.8	0.0200
25	79.8	0.1250
50	79.8	0.5000
75	79.8	1.1250
100	79.8	2.0000
150	79.8	4.5000
200	79.8	8.0000
250	79.8	12.5000
300	79.8	18.0000
500	79.8	50.0000
750	79.8	112.5000
1000	79.8	200.0000
1500	79.8	450.0000
2000	79.8	800.0000

NOTE—Brass is commonly examined at a magnification of 75 diameters. If the diameter of the inscribed circle is increased to 84.5 mm., or a rectangle having an area of 5,625 sq. mm. is used, the multiplying factor "f" becomes unity, and the number of grains in the larger circle is the same as the number of grains per square millimeter.

If grain size measurements are made on a rectangle, instead of with a circle, the method is practically the same as before. The number of grains in the inclosed area is increased by half the number of grains intersecting boundary lines, giving a close approximation to the total number of whole grains in the measured area. This number is then multiplied by the suitable factor from Table XXX to give the number of grains per square millimeter. The rectangle may be inscribed on the ground-glass screen of the camera, or the measurements may be made on a photomicrograph of known magnification.

Specifications sometimes require the grain size indicated in terms of the diameter of the average crystal in millimeters, or the area of the average grain in μ^2. The following formulas from Jeffries' paper give the methods of calculation:

z = completely included grains;
w = boundary grains;
x = equivalent number of whole grains in 5,000 sq. mm. (circle 79.8 mm. in diameter or rectangle with an area of 5,000 sq. mm.);
$x = \frac{1}{2} w + z$.
m = magnification;
f = multiplying factor used to obtain grains per sq. mm.; (See Table XXX);
$f = m^2 5{,}000$;
n = number of grains per square millimeter; $n = fx$.
d = average diameter of grain in millimeter; $d = 1/\sqrt{n}$
a = area of average grain in μ^2. $a = 1{,}000{,}000/n$

All that has been said with regard to the effects of work on brass applies to steel as well, and in fact the theory of amorphous material as suggested by Beilby and developed by Rosenhain was first applied to mild steel. The same is true of grain growth and grain size measurements except that the effects of slight temperature changes are not nearly so striking with steel as with the non-ferrous alloys like brass and bronze. Grain size measurement is seldom required in the specifications of worked steel, but grain count or grain size is a frequent requirement in the inspection of rolled or drawn brass in the form of sheet, tubes, rods and the like.

β-brass.—The striking appearance, due to the twinning of α-brass, which makes the measurement of grain size a comparatively easy matter, is almost wholly lacking in the class of brasses commonly known as the β-brasses, although in practice the great majority of them are mixtures of the α and β crystals. The best known example of the β-brass is Muntz metal, an alloy with approximately 60 per cent Cu and 40 per cent Zn. It has had an extended use in the industries, largely because it has many good qualities and is relatively cheap, but because of the readiness with which it undergoes local pitting and corrosion its use is gradually decreasing. One of the important uses of the metal has been in the production of condenser tubes and, in spite of its certain disadvantages, its use has by no means been discontinued. Figures 175 and 176 show the character of the β-mixture

as it is found in condenser tubes differing somewhat in composition. The tubes were subjected to a considerable amount of cold work in the process of drawing, so that, as is to be expected, the annealed tube shows the characteristic twinned structure of the α-brass crystals as they appear in the β-field. Under the action of alkaline hydrogen peroxide the α-brass takes on its usual brownish tint, while the β-crystals are practically unaffected or slightly yellow. The microscope shows, then, the manner of distribution of the two crystal forms, and gives to the metallographer an indication of the character and amount of heat treatment to which the tube has been subjected after its welding or drawing has been finished. β-brass is without definite crystal form, and does not twin under ordinary conditions, if at all.

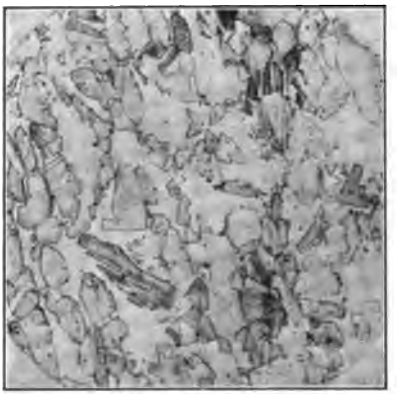


FIG. 175.—Twins of α-brass in a β-field. 75 ×.

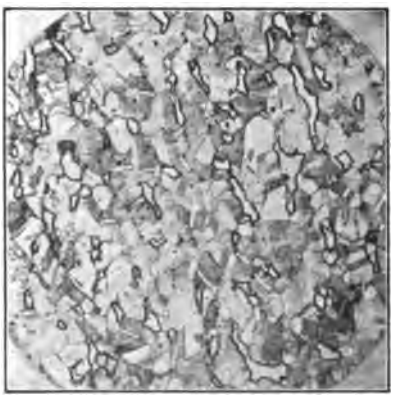


FIG. 176.—β-brass in field of twinned α-brass. 75 ×.

Since Muntz metal consists of two crystal forms, it is much more apt to segregate than ordinary α-brass, and here again the microscope can be of great service to the metal tester. A few illustrations taken from technical practice will illustrate the application of the microscope to defective material of this sort. Figure 177 shows the distinct layer formation in a condenser tube with α-brass above and irregular masses of yellow β-brass distributed through the α-field in the lower part of the photograph. This tube was etched with alkaline peroxide so

that the twinning of the α-crystals is plainly visible. Figure 178 illustrates another case of defective material in which the α-brass is irregularly distributed through the β-field. *A* is a specimen etched with ammoniacal ammonium persulfate, in which the island of light colored α-brass is distinctly visible in the field of β-brass, which has been colored almost black by the etching reagent. *B* is a part of the same tube, but etched with alkaline peroxide so that the brownish colored α is clearly marked in the field of yellow β.

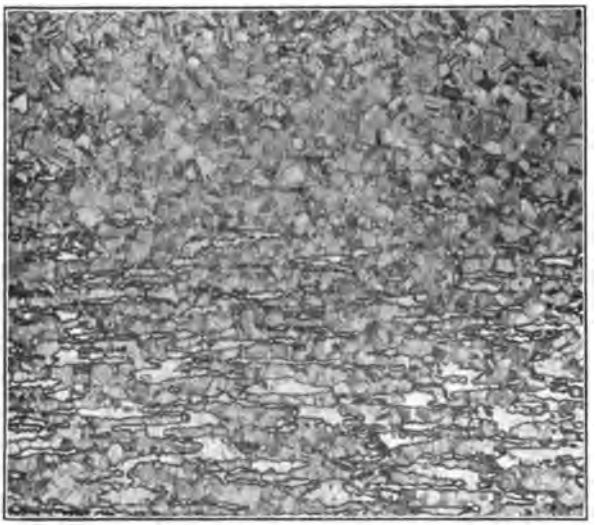


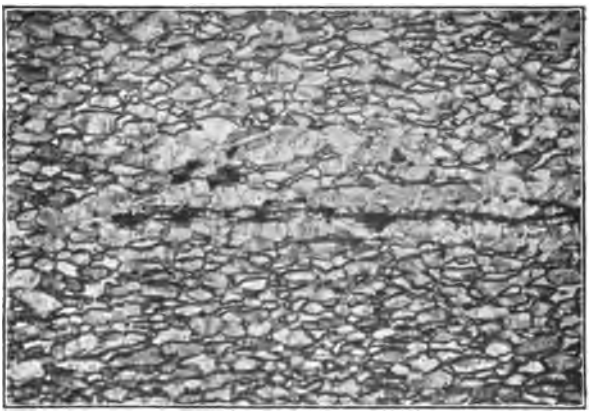
FIG. 177.—Layer formation in defective condenser tube showing α- and $\alpha + \beta$-layers. 75 ×.

The appearance and physical properties of β-brass vary over a great range, depending on the temperature to which the material is heated and on the way in which it is cooled after annealing. The following micrographs of Fig. 179 show some of the many forms in which β-brass occurs following variations in heat treatment. The chemical composition is the same in all four specimens.

Season Cracking.—Copper, brass, and bronze, when overstrained and not sufficiently annealed, are subject to a remarkable and dangerous action known as **season cracking.** If the

shell case, tube or other article, which has been subjected to severe cold work without the relief of annealing, is allowed to

A. Etched with NH_4OH and $(NH_4)_2S_2O_8$. α-brass very slightly attacked. 75 ×.

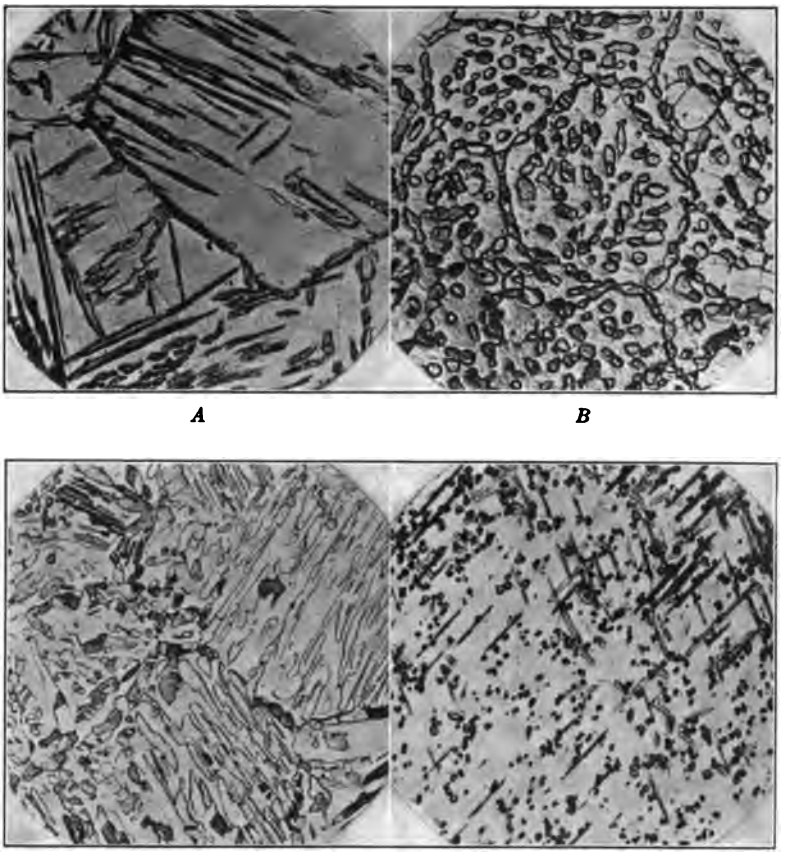


B. Part of the same tube etched with NH_4OH and H_2O_2. 75 ×.

FIG. 178.—Formation of islands of α-brass in β-field.

stand for some length of time, especially if the material is stored in a moist atmosphere or near salt water, a spontaneous decompo-

sition of the material takes place, leading to the formation of small or large "season cracks." Failure of brass and bronze parts from this cause has lead to serious damage and financial loss, so serious that the subject was investigated by the Bureau of Standards[1]



A *B*

C *D*

FIG. 179.—Muntz metal showing variations with heat treatment. 100 ×. (*Homerberg.*)

in connection with breaks in the Catskill Aqueduct, the Minneapolis Filtration Plant and some manganese bronze bolts used in the Panama Canal lock gates.

[1] Bureau of Standards *Technical Paper* No. 82, January, 1917.

While the detection of this difficulty is really a chemical rather than a metallographic problem, the question is one commonly left to the metallographer for solution. While the exact reagent to use and the method of applying the test is still a subject of discussion and much experimental work, the method as recommended by the Ordnance Department may be taken as representing the general nature of the test. The suspected material is immersed in an excess of a solution of 1.5 per cent mercuric chloride or mercuric nitrate, and if the overstrain has been severe the effects of "season cracking" are so greatly accelerated that cracks often leading to complete break down of the material may be started at once. It is generally accepted that if the material will stand immersion in the mercuric salt for a period of 4 hr., it may be considered free from those strains which would lead to season cracking, either during the interval of storing or during long continued use. The action of the mercury salt seems to be due to the deposition of metallic mercury and its diffusion into the metal at those places in which the amount of amorphous material is greatest.

Other Copper Alloys.—In addition to the common brasses and bronzes with which the metal tester usually has to deal, there are many more complex alloys whose mechanical characteristics, as far as their microscopic examination is concerned, are much the same as those of the commoner metals. **Admiralty metal,** for instance, is ordinary 70–30 brass in which from 1 to 1.5 per cent of the zinc is replaced by tin, making the alloy somewhat less readily corroded, and in **naval brass** the same substitution of tin is made in an alloy of the Muntz metal type for the same reason. In both cases the appearance of the resulting alloys is substantially the same as that of the corresponding common brasses, and

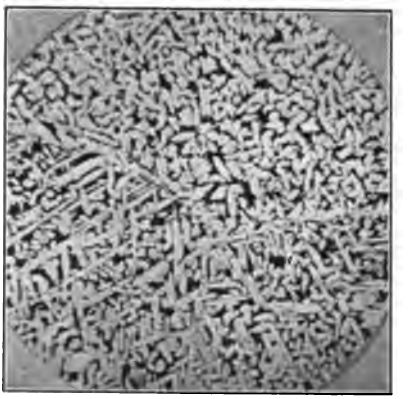


FIG. 180.—Aluminium bronze. 75 ×.

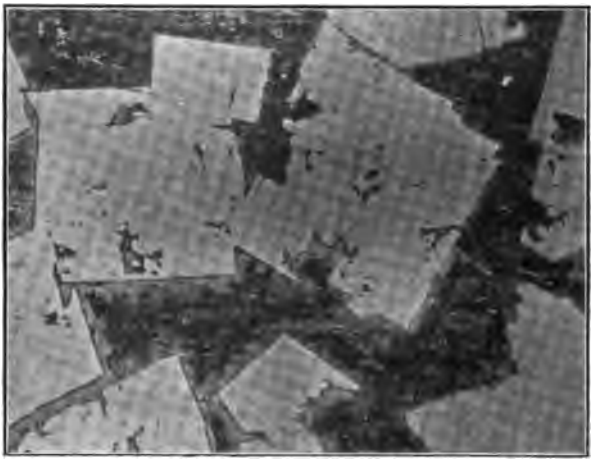
the effects of cold work and annealing are indicated in the same way as with the simpler alloys. **Aluminium bronze,** made by alloying copper with an amount of aluminium not exceeding 11 per cent, is sometimes submitted for examination. It is seldom used, except in the cast form, where it is characterized by the very irregular distribution of the dendritic crystals, which probably accounts for the high tensile strength and ductility of this material. Figure 180 shows the closely interlocked structure of cast aluminium bronze as compared with the much more open structure of phosphor bronze, shown on p. 457, Fig. 164.

Tin-antimony Alloys, Babbitt Metal and Other White Bearing Alloys.—The "white" alloys used for light bearings commonly

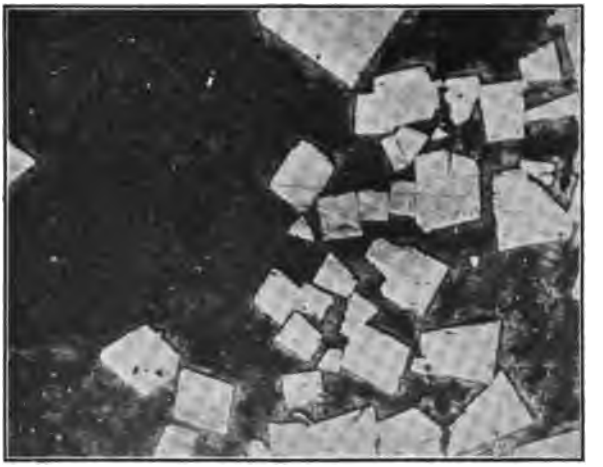
FIG. 181.—Antimony in a lead-antimony eutectic matrix. 75 ×. (*Homerberg.*)

contain tin, antimony and lead in varying amounts, often as in the case of Babbitt metal with the addition of copper. The characteristic feature of the group is the existence of the hard, cubical crystals of the compound SbSn which, in the case of Babbitt itself, is probably the material which gives to the alloy its valuable properties. In the simple lead-antimony alloys, less frequently used in practice, the hard material is composed of antimony crystals imbedded in the lead matrix. In either case the microscope is of great value in determining the regularity or irregularity of distribution of the hard grains in the soft matrix. Figure 181 shows the irregular shape and uneven distribution of

antimony crystals in the lead base of a badly-cooled, white bearing. In the case of the tin-antimony alloys, there is a marked



A



B

FIG. 182.—Variations in size and distribution of SbSn in white metal.

tendency for the SbSn crystals not only to vary enormously in size but also to segregate during the cooling of the melted alloy,

with results which are quite unsatisfactory, and yet are exceedingly difficult to detect by means other than microscope control. Figure 182*A* shows abnormally large crystals, while *B* in another part of the same casting shows not only comparatively small masses of the SbSn compound but also a most unequal distribution of the bearing material in the matrix. These photographs illustrate another characteristic of Babbitt metals which requires careful microscopic control, namely the influence of the cooling rate on the crystal size. The usual method of lining a bronze bushing with Babbitt metal is to pour the molten Babbitt in the cylindrical opening, left between the inner wall of the bushing to be lined and the outside of an iron or steel core. The factors which influence the distribution of the crystalline compounds in the lining are essentially the temperature of the iron core and the temperature of the bronze bushing. The latter temperature cannot be changed to any great extent, but the temperature of the core can, and should, be carefully regulated for the most successful results. The two crystals which separate from common Babbit are Cu_3Sn and SbSn. The size and character of each is largely determined by the temperature of the core against which the melted metal is poured. The effects of changing the cooling rate by changing the temperature of the mold are illustrated in the photomicrographs of Fig. 183. The alloy was the same in each case, and the temperature from which the metal was poured was carefully controlled, so that the only varying factor was the temperature of the oil-bath in which the receiving-tube was immersed. It is very evident that a marked difference in crystal size is produced by these temperature changes, and by determining the most favorable size for a given purpose it is possible to control the physical properties chiefly the frictional resistance of the material, within narrow limits. Metallographic control of Babbitt-lined bearings, both with regard to the crystal size and with regard to the evenness of distribution of the crystalline material, has been adopted as part of the testing routine of several large industrial plants engaged in making bearings.

It is hardly necessary to suggest that in sampling a material in which segregation occurs so commonly, and in which the size of the crystal masses may vary so widely, the microscope can be of great service to the chemist in the selection of a sample of suitable

size, from the right location in the specimen to be tested, so that the analysis may truly represent the composition of the metal.

Finally, the danger of overestimating the value of the microscope must be emphasized. The microscope is a valuable, and

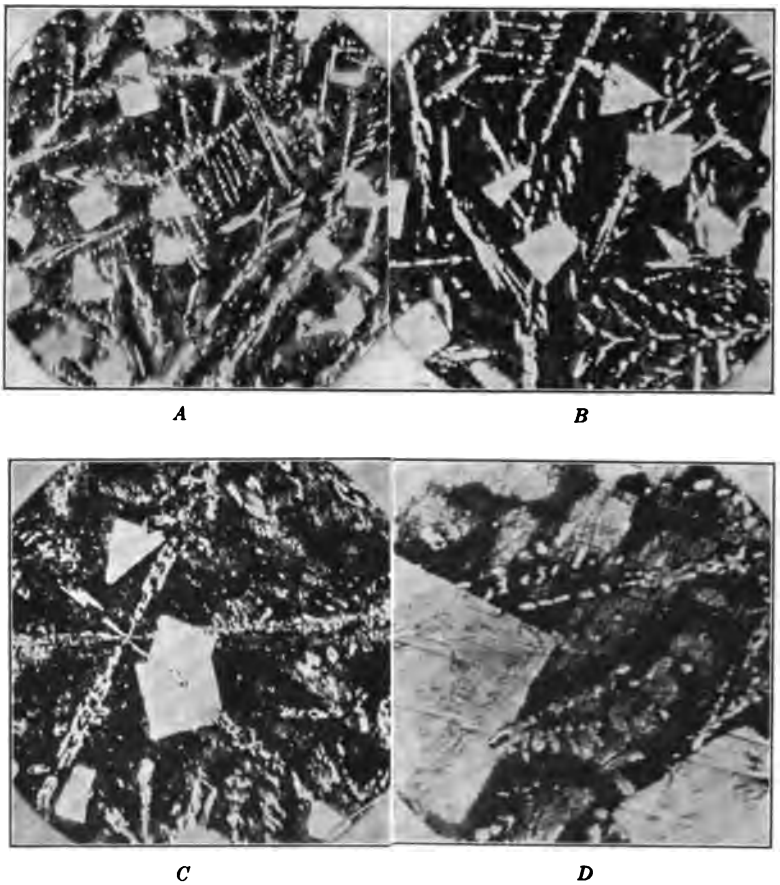


FIG. 183.—Babbitt metal showing effect of cooling rate on crystal size. 75 ×. (*Federhen.*)

in some cases an indispensable, tool for the metal tester, but the inexperienced metallographer must realize fully that the correct interpretation of microscopic appearances in doubtful cases needs much practice and experience with metals under widely-differing

conditions of composition, heat and mechanical treatment. The microscope should always be considered as but one of the means available for the inspection of metals and alloys. It is most certainly true that the value of proper sampling in technical work has not been properly recognized or appreciated, and it is evident that the microscope can be of great value in many cases in getting samples which are really representative.

Quite often, in practice, the chemist in charge of an analytical laboratory, who is responsible for the accuracy of the results, has nothing whatever to say about the way in which the samples submitted to him for analysis shall be taken. He can assume the responsibility for correct chemical analyses, but cannot guarantee that the values given for different constituents actually represent the average composition of the material, since, as has been shown, **the composition of the sample is not necessarily uniform throughout its entire cross-section, but is often quite the reverse.**

For this reason, judgment based on chemical analysis alone is not always correct as the analytical results are influenced to a marked degree by the methods of sampling. Control analyses, made by different chemists on borings from the same piece, are of value only when the sample to be analyzed has been shown by the microscope to be homogeneous, or at least uniform throughout its whole cross-section. Much of the disagreement among chemists has no doubt been due to incorrect sampling with the resulting lack of uniformity in the samples analyzed. It has been remarked[1] that "The one great argument against the use of chemistry for the grading of iron has been that the work of the chemists varied so much that it was impossible to obtain anything like uniform results." That the chemist has been responsible for these conditions to a very limited extent has been shown. Irregularities in the chemical composition of the sample, due to local segregation, are often far greater than the possible errors of analysis. This is true not only of pig iron but also of all other kinds of iron and steel and, to a less degree, of the brasses, bronzes and other non-ferrous alloys. Metallography is of great value to the chemist in helping him to detect these local differences, and indeed it is impossible to determine such differences in many cases except by the microscope.

[1] H. E. FIELD, *Iron Trade Review*, February, 1903.

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